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Rare-Earth Quinolinates: Infrared-Emitting Molecular Materials with a Rich Structural Chemistry

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Near-infrared-emitting rare-earth chelates based on 8-hydroxyquinoline have appeared frequently in recent literature, because they are promising candidates for active components in near-infrared-luminescent optical devices, such as optical amplifiers, organic light-emitting diodes, ... Unfortunately, the absence of a full structural investigation of these rare-earth quinolinates is hampering the further development of rare-earth quinolinate based materials, because the luminescence output cannot be related to the structural properties. After an elaborate structural elucidation of the rare-earth quinolinate chemistry we can conclude that basically three types of structures can be formed, depending on the reaction conditions: tris complexes, corresponding to a 1:3 metal-to-ligand ratio, tetrakis complexes, corresponding to a 1:4 metal-to-ligand ratio, and trimeric complexes, with a 3:8 metal-to-ligand ratio. The intensity of the emitted near-infrared luminescence of the erbium(III) complexes is highest for the tetrakis complexes of the dihalogenated 8-hydroxyquinolinates.

Introduction

There is a growing interest to replace the traditional inorganic optoelectronic components in optical amplifiers by organic molecular materials, because of advantages such as solution processing, flexibility, and low cost. Whereas organic materials emitting in the visible region have already taken their place in the display application field, the development of organic materials emitting in the near-infrared region has only started recently, stimulated by innovations in communication network technology.

One class of materials that has been studied as near-infrared-emitting organic compounds are the rare-earth quinolinates (REQs). Historically, 8-hydroxyquinoline (8-quinolinol) has been used as a reagent for gravimetric analysis, because of its excellent complexing properties with a wide range of metal ions, including the rare earths, and because of the low solubility of the resulting complexes in aqueous media.[1,2] It has also found applications as an extr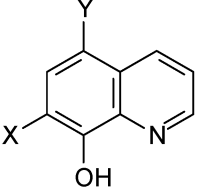action reagent.[3−11] The most intensively investigated metal complex of 8-hydroxyquinoline is tris(8-hydroxyquinolinato)-aluminum(III),[12−19] because this complex exhibits an intense green electroluminescence and performs well as the active component in organic light-emitting diodes (OLEDs) operat-

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Chart 1. Quinolinol Ligands Discussed in This Article

Name	X	Y	Abbreviation
8-quinolinol	H	H	HQ
5-chloro-8-quinolinol	Cl	H	HQ5Cl
5,7-dichloro-8-quinolinol	Cl	Cl	HQ57Cl
5,7-dibromo-8-quinolinol	Br	Br	HQ57Br
5,7-diiodo-8-quinolinol	I	I	HQ57I

ing in the visible region.[20,21] Derivatives of 8-hydroxyquinoline have also been used as building blocks for supramolecular coordination compounds.[22,23]

It has been assumed that complexes of 8-hydroxyquinoline with rare earths are tris complexes (the metal-to-ligand ratio is 1:3),[1,24−33] adducts of 8-hydroxyquinoline to these tris complexes,[4,34] or tetrakis complexes.[4] Several authors noticed that it is very difficult to obtain analytically pure tris complexes.[3,35−38] The 8-hydroxyquinolinate complexes of neodymium(III), erbium(III), and ytterbium(III) are particularly interesting, because of their infrared luminescence,[30−31,39−41] and because they can be used for the fabrication of near-infrared-emitting OLEDs.[42−47] These OLEDs can be applied in optoelectronic devices.[48,49] An

important issue in the design of near-infrared-emitting lanthanide complexes is to avoid water molecules from binding to the lanthanide ion. By designing bulky ligands, a "cage" can be formed around the lanthanide which excludes water from the first coordination sphere.[50] In that way, even water-free complexes with only three bidentate ligands can be formed.[51] Given the efforts that physicists put into the design of devices based on rare-earth complexes of 8-hydroxyquinoline, it is very surprising that hardly anything is known about the structure of these compounds. Only one crystal structure of a rare-earth complex of 8-hydroxyquinoline is available in the Cambridge Crystallographic Database, and the complex described is a trinuclear species: $[Yb_3(C_9H_6-NO)_8 \cdot (CH_3COO)] \cdot 3CHCl_3$.[52]

In this study, we show that complexes of rare earths with 8-hydroxyquinoline and its halogen-substituted derivatives possess a rich coordination chemistry. Depending on the ligand and the reaction conditions, we could isolate and characterize at least three different types of complexes: (1) hydrated tris complexes, $LnQ_3 \cdot xH_2O$, (2) tetrakis complexes, $BLnQ_4$, and (3) trimeric complexes, Ln_3Q_8A. Here Ln is a rare-earth ion, Q is the deprotonated form of 8-hydroxyquinoline or a derivative thereof, A is a monovalent anion, and B is a monovalent cation. Monomeric anhydrous tris-(8-hydroxyquinolinato)lanthanide(III) complexes seem to be nonexistent; at least they could not be obtained from solvent syntheses. The results are interpreted in terms of the large size of the rare-earth ion striving to a high coordination number, in terms of the solubility of reaction intermediates, and in terms of the substituents on the parent 8-hydroxyquinoline ligand. In Chart 1, a summary of the ligands that have been used in this study is shown, together with the abbreviations that will be used throughout this Article.

Results and Discussion

A. Reinvestigation of Synthetic Procedures from the Literature. Several literature procedures for the synthesis of rare-earth quinolinates have been described. In most cases, the authors assume that the resulting complexes correspond to the general formula LnQ_3, with Ln being a rare-earth ion

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and Q being the deprotonated quinoline derivative. We have taken the most frequently used literature procedures to synthesize rare-earth quinolinates, and consequently, we have analyzed the reaction products formed by each synthetic procedure. The outcome of nearly every synthetic procedure described consists of mixtures of different species. Using mass spectrometry, CHN elemental analysis, ^{1}H NMR spectrometry, and single-crystal X-ray structure determination, we have succeeded in the identification of the different species present in these mixtures. In what follows, a short description of the most frequently used literature procedures is given, including the analysis results of the reaction products. A detailed explanation of why one type of reaction product is always seen with a specific set of reaction conditions is given in part C of this Article (Rationalization of the Results).

The first procedure, which will be denoted as method A throughout this Article, was described in 1971.[27] A solution of HQ in ethanol is added to a solution of rare-earth nitrate in water. After addition of a slight excess of a basic solution (ammonium hydroxide solution), the complex precipitates. We applied this method to nearly every trivalent rare-earth ion, and the resulting compounds gave CHN analyses which generally did not match the 3:1 ratio. Instead, the measured carbon content proved to be too low (when compared to that of a calculated water-free structure). For some of them, adding one or two water molecules to the calculated structure gave satisfactory CHN results, and as a consequence, simply looking at elemental analysis data could lead to the conclusion that the complexes correspond to the general formula $LnQ_3 \cdot xH_2O$, with x being 1 or 2. This is also the case for samples **1** and **2** (Table S1 in the Supporting Information), which were synthesized by method A (or a slightly altered version thereof). However, analysis of a diamagnetic yttrium-(III) sample by ^{1}H NMR spectrometry showed a whole range of peaks, indicating the presence of more than one species in solution. Moreover, mass spectrometry did not confirm the formation of pure LnQ_3 either. Instead, the most prominent peaks in the mass spectrum suggested the presence of a trimeric species, corresponding to the general formula $Ln_3Q_8{}^+$, with Ln being a trivalent rare-earth ion and Q being (deprotonated) 8-hydroxyquinoline. Repetition of this analysis showed identical results, also with different rare-earth ions used.

Single crystals of complex **2** could be obtained, which had been synthesized using a slightly altered version of method A, in which ethanol instead of water was chosen to dissolve the $ErCl_3 \cdot 6H_2O$. X-ray analysis of these crystals proved the presence of a trimeric species, the structure of which is shown in Figure 1. In this structure, two peripheral erbium ions each coordinate to four quinolinate ligands. An additional hydroxide anion coordinates to one of the peripheral erbium ions, while a water molecule is coordinated to the other one. Each quinolinol ligand coordinates in a bidentate fashion and bridges the erbium ions via the oxygen atom except for two peripheral ligands.

The second method, method B, was reported in 2001.[47] Here, the complex is precipitated without addition of a base,
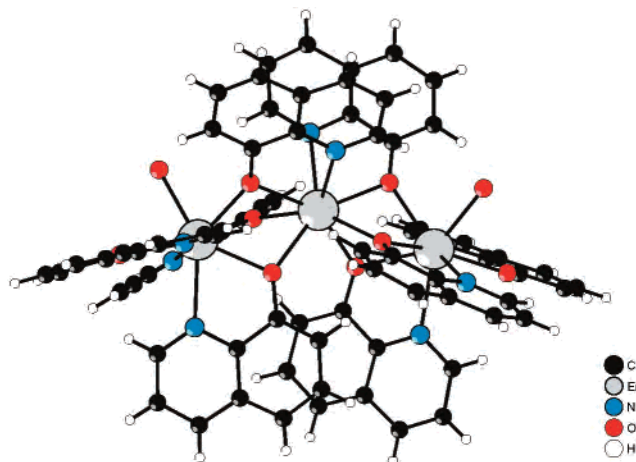

Figure 1. Crystal structure of $NH_4[Er_3(Q)_8]Cl(OH)\cdot4C_4H_8O_2$ (**2**). For clarity, solvent molecules (dioxane) have been omitted.

adding the rare-earth chloride in water to a quinolinol solution in a water/methanol (20/80) mixture. The complex precipitates after one night of stirring. The analysis of this procedure is especially relevant, since many researchers working in the field of OLEDs use this synthetic procedure to make their active emitting materials.[42−47] The elemental analysis results of an yttrium(III) complex, **3**, synthesized by this method are displayed in Table S1. Again, the amount of carbon is underestimated (when compared to that of the calculated water-free structure). The mass spectrum of this complex was very similar to the one discussed in the previous paragraph. Given the similarities between the analytical results obtained by using method B and method A, it can be concluded that, here, trimeric species are formed as well.

We used the next method, method C (see also further text), to synthesize rare-earth complexes of HQ and HQ5Cl.[25] This method uses ammonium acetate as a base and water as the solvent for the rare-earth salt and acetone to dissolve the ligand. Here also, evidence for the presence of trimeric species was found. Single crystals of compound **4** were analyzed by X-ray diffraction techniques and indeed proved the existence of a trimeric complex, although it differs somewhat from that described in Figure 1, because one acetate ion is bound to the central erbium ion. The reason we used the 5-chloro-substituted ligand is the higher solubility of the resulting complex in solvents suitable for the growth of single crystals. The structure can be seen in Figure 2. It is very similar to the one (and only) described in the literature:[52] the two peripheral erbium ions are surrounded by four Q5Cl ligands each. A third erbium ion acts as a linker between these two moieties, resulting in a trimeric unit. This third erbium ion is coordinated to six ligand oxygens and a chelating acetate counterion.

We also synthesized complexes of HQ57Cl, HQ57Br, and HQ57I following method C.[25] To a solution containing the rare-earth chloride were added ammonium acetate and an excess of the ligand in acetone. The elemental analysis results of complex **5** are given in Table S1. It shows that this complex behaves in a different way compared to those derived from unsubstituted 8-hydroxyquinoline. This was also evidenced by the mass spectra and the NMR spectra.
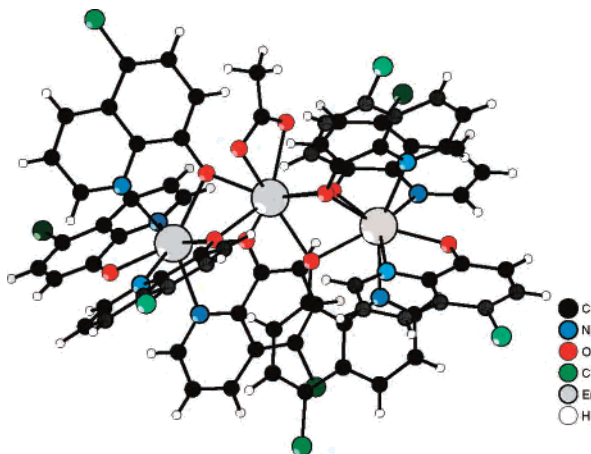
Figure 2. Crystal structure of $Er_3(Q5Cl)_8(CH_3COO)\cdot 6CHCl_3$ (**4**). For clarity, solvent molecules (chloroform) have been omitted.
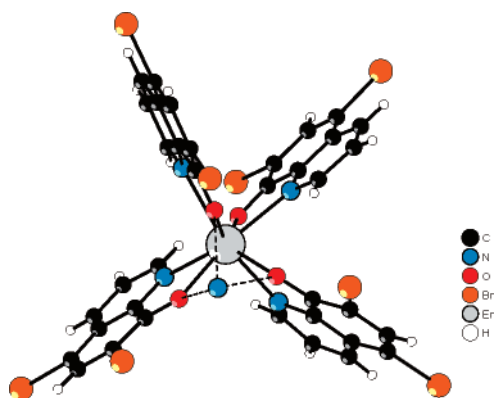

Figure 3. Crystal structure of $NH_4[Er(Q57Br)_4]\cdot C_4H_8O_2$ (**5**). The dashed lines indicate the coordination of the ammonium ion. For clarity, solvent molecules (dioxane) have been omitted.

Here, we no longer have trimeric species, but dimerized tris complexes on one hand, and tetrakis complexes on the other hand. We were able to crystallize the tetrakis form, the structure of which is shown in Figure 3. This is the first known structure of a tetrakis rare-earth quinolinate complex. In this structure, the erbium ion is surrounded by four Q57Br ligands, resulting in a coordination number of eight. Three of the ligands are oriented with their oxygen atoms toward the ammonium counterion, which is hydrogen bound to these three oxygen ligand atoms (N⋯O distances 2.669(10), 2.675-(12), and 2.738(11) Å). The oxygen atom of the fourth ligand is oriented in the opposite direction.

Next we used method A in combination with the dihalogenated ligands.[27] The CHN analysis results of the erbium complex **7** are also incorporated into Table S1. They correspond to a tris/tetrakis mixture, which was also evidenced by mass spectrometry and ^{1}H NMR. We were able to crystallize the tris component, the structure of which is shown in Figure 4. This is the first and—up till now—only evidence of a crystal structure where only three quinolinol ligands are bound to a rare-earth ion. The erbium coordination consists of three Q57Cl ligands together with two water molecules. These water molecules form strong hydrogen bonds (O⋯O distances 2.661(10) and 2.740(11) Å) to the oxygen atoms of two ligands of a second tris complex.
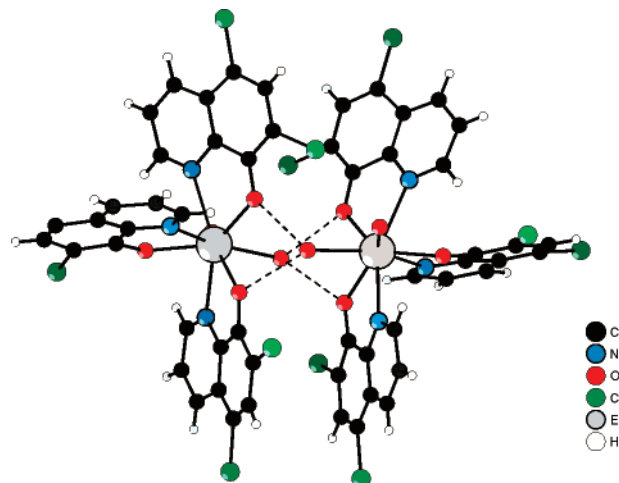

Figure 4. Crystal structure of $Er(Q57Cl)_3\cdot 6C_4H_8O_2$ (**7**). For clarity, solvent molecules (dioxane) have been omitted.

B. Improved Methods. It has been shown that using HQ and HQ5Cl resulted in the formation of mainly trimeric complexes, whereas the use of HQ57Cl, HQ57Br, and HQ57I resulted in the formation of tris/tetrakis mixtures. Having concluded that most literature procedures do not give easy access to pure species, we made considerable efforts to adapt some of these methods to improve the purity of the resulting precipitates.

Pure tetrakis complexes could be obtained by using the sodium salt of the ligand in ethanol. This is the case for all ligands, including unsubstituted and 5-chloro-substituted ligands. A typical example is incorporated into Table S1: complex **8**, consisting of an ytterbium(III) ion bound to Q5Cl ligands.

The best results for tris-coordinated structures were achieved by using as little ammonium hydroxide as possible and dichloromethane and water as the solvents (two-phase system). Mixtures with up to 75% of tris complex could be obtained using this method, as was the case with compound **10**, which is an yttrium(III) complex of Q57Cl.

No improved method for the formation of pure trimeric species was found, since at a later stage it was proved that method B resulted in the formation of virtually pure trimeric complexes (90+%; see further text). When the CHN values for compound **3**, which was synthesized by method B, are recalculated for a trimeric structure (see Table S1, "improved methods"), a good match is found between the calculated and the observed values.

The crystallographic data for the crystal structures of complexes **2**, **4**, **5**, and **7** can be found in Table S2 in the Supporting Information.

C. Rationalization of the Results. We observed that, depending on the reaction conditions (solvent, base) and on the ligand used, different species are formed. In Scheme 1, we have summarized the processes leading to one or another structural specimen. The mechanisms behind these processes are suggested below.

a. Formation of Tris and Tetrakis Complexes. Pure tetrakis complexes could be obtained with Q57Cl and hydrated yttrium(III) chloride following the improved syn-

Scheme 1. Summary of Rare-Earth Quinolinate Structural Chemistry[a]
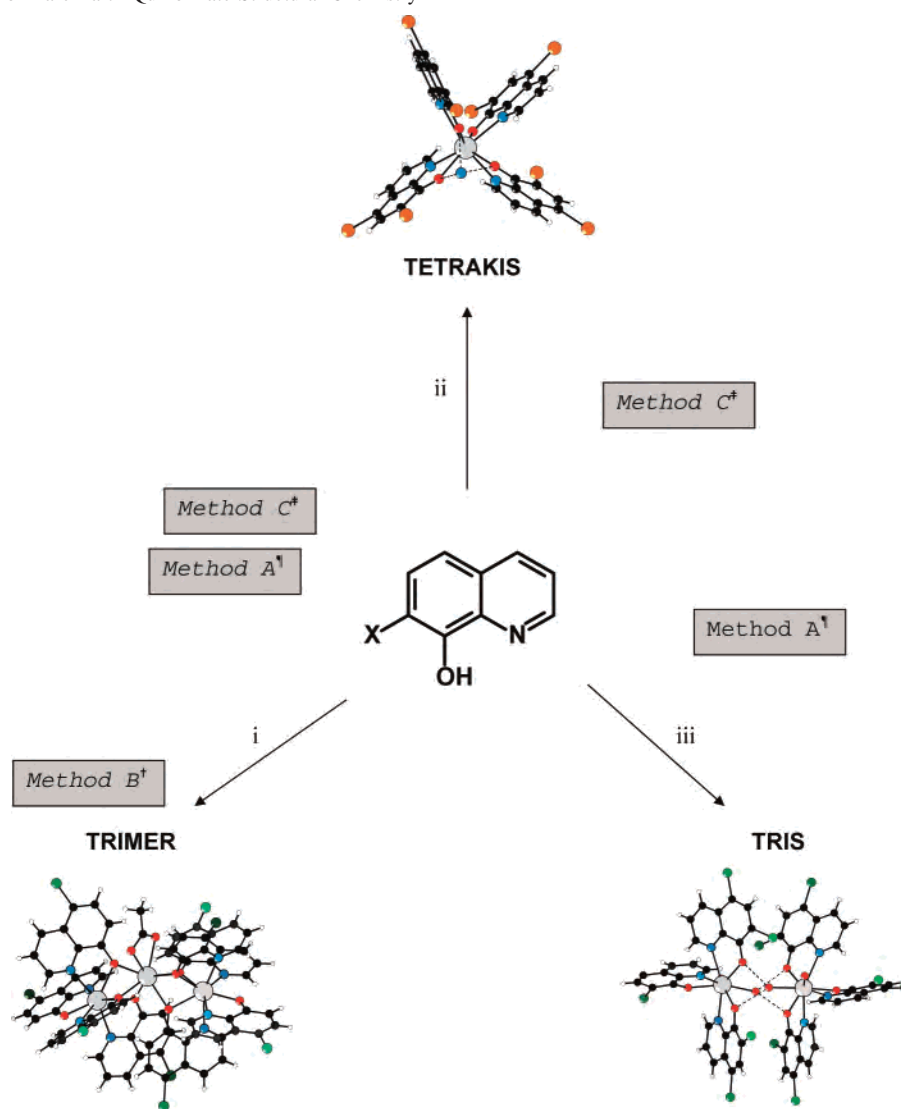
[a] (i) Trimeric species are formed only when X = H, in the absence of small cations. (ii) Tetrakis species can be formed for X = H or a halogen. Na^{+} ions give pure species. NH$_4$[+] gives mixtures. (iii) Tris species are formed for X = halogen and with as few cations as possible. (‡) Method C[25] gives a mixture of trimer and tetrakis when X = H and a mixture of preferentially tetrakis and some tris when X = halogen. (¶) Method A[27] gives a mixture of trimer and tetrakis when X = H and a mixture of preferentially tris and some tetrakis when X = halogen. (†) Method B[47] gives virtually pure trimer.

thetic procedure using the sodium salt of the ligand. The ^{1}H NMR spectrum of compound **9** is shown in Figure 5a, whereas the elemental analysis data are included in Table S1. As seen in the ^{1}H NMR spectrum, only one set of resonances is observed, implying the presence of only one complex in the solution. The resonances are shifted ca. 0.1– 0.2 ppm compared to those of the free ligand. To check whether the tetrakis complex is in equilibrium with the trimeric or the tris complex, variable-temperature NMR spectra were recorded. Heating the sample of tetrakis complex to 373 K in DMSO-d_6 solution did not result in the appearance of any new peaks, and no observable changes in the NMR spectrum could be detected. No equilibrium is observed in solution, since this would be evidenced by the presence of an additional set of peaks in the NMR spectrum. From the mass spectral data, and from NMR and CHN data, it can be concluded that the complex is a pure tetrakis complex.

Using method C, one obtains a mixture of tetrakis and tris complexes. This can be understood from the NMR spectrum in Figure 5b (compound **6**), in which two additional sets of peaks are present, proving the presence of three different species in solution, one of which has been identified as the pure ligand (small amount) and the other one as the tris species. The mass spectrum contains both tris and tetrakis peaks.

The altered method A results in the formation of the same species, but in different proportions, as can be seen in the NMR spectrum in Figure 5c (compound **10**). Here, the tris species is more abundant than the tetrakis species.

The driving force for the formation of the tetrakis species involves most likely (i) the solubility of the ligand and the resulting complex in a certain solvent and (ii) the presence of specific cations. Using HQ57Cl, which is soluble in ethanol, with a large excess of ammonium ions in slightly basic conditions, results in the formation of tris/tetrakis
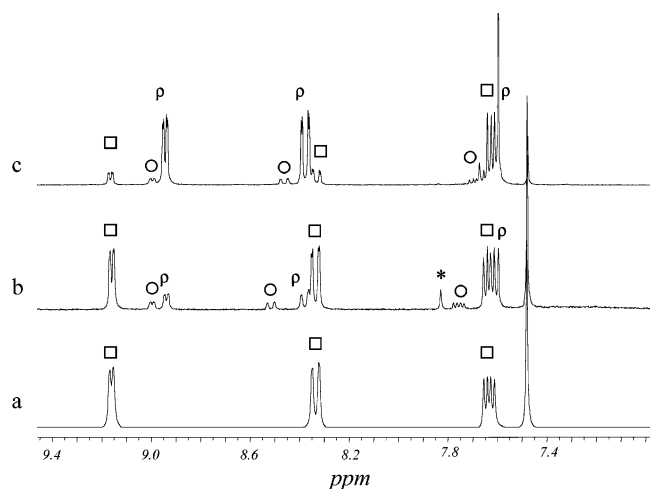
Figure 5. ¹H NMR spectrum of (a) compound **9**, (b) compound **6**, and (c) compound **10**. Resonances from the tetrakis species are marked by □, those from the tris species by ρ, and those from the free ligand by ○. The signal marked by * originates from the ammonium ion that was present in the tetrakis complex **6**.

mixtures. Using the same system, but with sodium ions instead of ammonium ions, results in the formation of pure tetrakis complexes.

Most likely, the synthetic routes toward tetrakis complexes involve the creation of both tris and tetrakis complexes. In the case of the tetrakis complexes containing the sodium cations, the complexes are poorly soluble in ethanol and precipitation of these species occurs fast, while the tris complexes remain in solution. This was proven by evaporating the solvent and examining the resulting residue by NMR and mass spectrometry.

The tetrakis complexes containing ammonium ions are better soluble in ethanol, which is evidenced by the absence of a precipitate after the same reaction time. After evaporation of the solvent and after analysis of the residue by NMR and mass spectrometry, both tris and tetrakis complexes could be identified.

b. Formation of Trimeric Complexes. The reaction of HQ or HQ5Cl with rare-earth ions gives trimeric complexes under most reaction conditions. However, several factors determine the outcome of the reaction. The *first factor* is the presence of small cations (sodium, ammonium) in solution. The structure of the tetrakis species contains a "cavity" in which these small cations can easily fit. In Figure 3, this cavity contains an ammonium cation (indicated by the dashed lines). In Figure S5 of the Supporting Information, a space-filling model showing this cavity can be found. In the absence of small cations, the rare-earth ions can take the role of cation to compensate the negative charge of the tetrakis moiety. Because of the trivalent charge of the rare-earth ion, two tetrakis moieties attach to a third rare-earth ion, which leaves one positive charge remaining. There is a competition between the small cations and the rare-earth ions to bind in the cavity of the tetrakis moieties, resulting in a mixture of both tetrakis and trimeric species. If bidentate anions are present (acetate, nitrate), these will compensate the remaining positive charge of the trimeric species by binding to the central rare-earth ion, leading to the formation

of the structure in Figure 2. If no bidentate anions are present, the structure in Figure 1 will be formed. Here, the central rare-earth ion of the trimer is bound via the nitrogen atoms of two quinoline ligands as well, whereas the oxygen atoms of these ligands are bridging the outer and central rare-earth ions. The *second factor* is steric hindrance by substituents in the 7-position of the quinoline moiety. If bulky halogen atoms (Br, I) are present in this position, the cavity size is too small to incorporate bulky rare-earth ions, resulting in the fomation of a mixture of tris and tetrakis complexes. The *third factor* is the composition of the solvent mixture used in the synthesis. This should be chosen in a way that allows slow precipitation of the resulting complex. Using large quantities of water causes immediate precipitation of every species being formed, because of the poor solubility. This would prevent the isolation of pure species. The best results to obtain pure trimeric species were obtained by method 2, which uses a mixture of water and methanol in a 20:80 ratio, and an excess of ligand. Since no sodium or ammonium acetate is used as base, the ligand itself plays the role of base, and a structure similar to the one shown in Figure 1 is formed. Apart from the X-ray analysis of the structure in Figure 1, the identity of this trimeric species was confirmed by a full 2D COSY and NOESY NMR study of the diamagnetic yttrium(III) sample **3**, which is available as Supporting Information (Figure S6).

D. Spectroscopic Investigation. A spectroscopic study has been conducted, to investigate if one structural species has better luminescent properties than another, and if the pure complexes have spectroscopic advantages over the mixtures or if one can just as well use the mixtures obtained by the most common synthetic methods to obtain sufficiently efficient emitting materials.

The erbium complexes of 8-hydroxyquinoline and its derivatives have received their share of attention as well.[30−31,39−41] We showed earlier that the halogenated quinolines yield stronger emitting complexes than the unsubstituted 8-hydroxyquinoline (replacing protons by halogen atoms yields a lower stretching vibration frequency in the C−halogen group than in the C−H group, reducing its quenching potential).[31] However, at that time, our knowledge of the structural chemistry of the rare-earth quinolinates was still not fully complete, and here, we can put these earlier findings in a broader perspective. For the current spectroscopic study, the following samples have been selected: (a) the tetrakis complex of HQ57Cl, Na[Er(Q57Cl)$_4$]·¹/$_2$H$_2$O, compound **11** in Table S1, (b) compound **12**, synthesized by the altered method A, containing about 75% of the tris complex of HQ57Cl, [Er(Q57Cl)$_3$]$_2$·2H$_2$O, and a small fraction of tetrakis species, (c) the tetrakis complex of HQ5Cl, Na[Er(Q5Cl)$_4$]·H$_2$O, compound **13**, (d) the tetrakis complex of unsubstituted HQ, Na[Er(Q)$_4$]·¹/$_2$H$_2$O, compound **14**, and (e) the trimeric species [Er$_3$(Q)$_8$]Cl·3H$_2$O, compound **15**.

First, a comparative study was performed in DMSO solutions. These solutions were prepared to absorb equal amounts of light at the same wavelength, corresponding to the maximum in the absorption spectrum of the complexes

Table 1. Relative Intensities and Radiative Lifetimes τ of the Near-Infrared Luminescence of Selected Erbium Complexes (DMSO Solution, Room Temperature)[a]

compd	structure	$\tau/\mu s$	rel intens
11	$Na[Er(Q57Cl)_4] \cdot {}^1/_2 H_2O$	2.3	1.54
12	$[Er(Q57Cl)_3]_2 \cdot 2H_2O$	2.2	1.45
13	$Na[Er(Q5Cl)_4] \cdot H_2O$	1.6	1.22
14	$Na[Er(Q)_4] \cdot {}^1/_2 H_2O$	1.5	1.00
15	$Na[Er_3(Q)_8]Cl(OH) \cdot 2H_2O$	1.6	1.08

[a] The excitation wavelength was 400 nm for the steady-state measurements and 355 nm (third Nd:YAG harmonic) for the time-resolved measurements. The concentration c was about 10^{-5} mol L^{-1}.

(which is centered around 400 nm, corresponding to one of the $\pi \rightarrow \pi^*$ transitions of the quinoline ligands). The erbium ion is sensitized by the quinoline ligands: the blue excitation light is absorbed by the ligands and transferred toward the erbium ion, which in turn emits it as near-infrared light (corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition). Using identical experimental settings (slit width, integration time, excitation wavelength, sampling interval), direct comparison of the integrated intensity of the near-infrared luminescence of each sample was possible. In Table 1, an overview of the relative intensities is given. In this table, the luminescence intensity of the erbium tetrakis complex with unsubstituted HQ, compound **14**, has been set to 1.00. When compounds **14**, **13**, and **11**, which are tetrakis complexes with HQ, HQ5Cl, and HQ57Cl, respectively, are compared, it is clear that the old adage is still valid: halogen substitution increases the luminescence intensity in erbium quinolinates in DMSO solution. It has to be noted that, in our earlier study, the "Er(Q)₃" sample had been synthesized according to method A and thus most likely consisted of a mixture of trimeric and tetrakis species. The "Er(Q57Cl)₃" and the "Er(Q57Br)₃" complexes from the same study had been made by the modified method A and thus most likely contained (mainly) tris and tetrakis species. As can be seen in the present study, the intensity difference between the trimeric and the tetrakis species of the same ligand is minimal (compounds **14** and **15**), whereas the tris species is somewhat less intense than the tetrakis species of the same ligand (compounds **12** and **11**). This explains why the halogenation only resulted in an increase of 30% in our earlier study, whereas in the present study, it is even more (about 50%).

A second feature which becomes apparent from looking at Table 1 is the fact that, although water molecules are bound directly to the erbium(III) ions in the structure of the tris complex **12** (see also Figure 4, complex **7**), the intensity difference between the tris and the tetrakis species is much less than would be expected (the tetrakis species not having any coordinated water molecules). It has to be noted, however, that these studies have been conducted in DMSO solutions. DMSO is known to repel water molecules from the first coordination sphere and to coordinate to the rare-earth ion itself. The S=O stretching vibrations are less efficient quenchers of the erbium luminescence than the O—H vibrations of the water molecules, and as a result, the intensity of the tris complex is not quenched significantly. To check the effect of the DMSO coordination, we dissolved
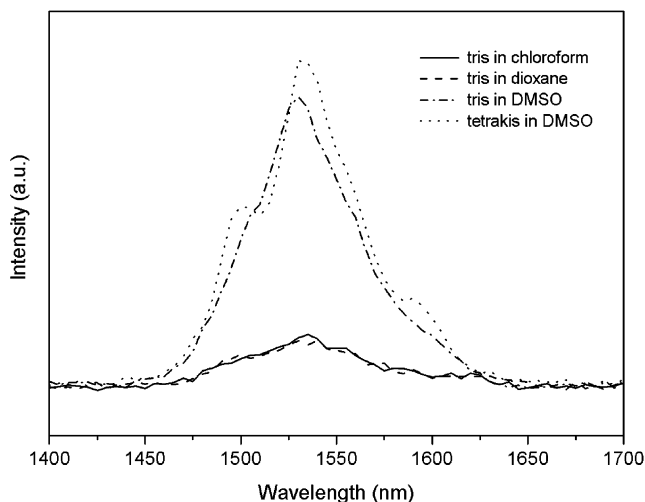

Figure 6. Combined luminescence spectra of erbium(III) complexes derived from HQ57Cl, indicating the effect of the solvent on the luminescence intensity of the tris species. Compound **12** is denoted as tris, whereas compound **11** is denoted as tetrakis. All solutions were isoabsorptive.

the tris complex in two different solvents: dioxane and chloroform, which are not able to repel the water molecules from the first coordination sphere. The effect on the luminescence intensity is obvious from Figure 6: the intensity of the tris complex in dioxane or chloroform drops down to only 20% of the intensity of the tris complex in DMSO. For the sake of comparison, the intensity of the tetrakis complex has been included in the figure as well. The tetrakis complexes are almost insoluble in both dioxane and chloroform, and thus, no comparative spectra could be recorded of the tetrakis complexes in these solvents. However, it can be assumed that the effect would be minimal, because of the efficient shielding of the erbium(III) ion by the four quinolinate ligands.

Conclusion

In this study, we explored the complex structural chemistry of the rare-earth quinolinates. The lack of insight into the processes determining the outcome of the synthetic procedures to make the rare-earth quinolinates has long hampered new breakthroughs in the use of these materials in near-infrared-emitting devices. One conclusion is that obtaining pure and anhydrous LnQ₃ is virtually impossible. Most synthetic methods to obtain rare-earth quinolinates yield a mixture of different species: hydrated tris complexes, tetrakis complexes, and trimers. Methods can be adapted to give a higher percentage of one or the other species, or even to obtain pure species. Although it had already been pointed out by several authors in the past that obtaining pure complexes is difficult, this study provides a crucial step forward in the understanding of the complex coordination chemistry of rare-earth quinolinates. This could give new insights into the application of these materials as near-infrared emitters in OLEDs or optoelectronic devices. The most intensely emitting erbium complexes are the tetrakis complexes of the 5,7-dihalo-8-hydroxyquinoline ligands (halo = chloro, bromo, or iodo). The synthetic methods toward rare-

earth quinolinates described in the literature do not give access to these tetrakis complexes in their pure form. As a consequence, this study offers the possibility to yield the most intensely emitting rare-earth quinolinates presently available.

This study involves only the trivalent rare-earth ions with small ionic radii (i.e., the second half of the lanthanide series, starting from Gd^{3+}, to Lu^{3+}, and including Y^{3+}, which is comparable in size to Ho^{3+}). At this moment, we are extending our study toward the larger lanthanide ions (La^{3+} to Eu^{3+}), and although there are several similarities in the structural behavior of the quinolinol complexes of these large ions, we have reason to believe that the full story includes even more structural variants than the three (trimer, tris, and tetrakis) discussed in this Article.

Experimental Section

Standard Techniques. CHN elemental analyses were performed on a CE Instruments EA-1110 elemental analyzer. ^{1}H NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer, operating at 300 MHz. Mass spectrometry was done on a Thermo Finnigan LCQ mass spectrometer. Electron spray ionization was used as the ionization process.

Spectroscopy. The steady-state luminescence spectra and the lifetime measurements were done on an Edinburgh Instruments FS920P near-infrared spectrometer, with a 450 W xenon lamp as the steady-state excitation source, a double-excitation monochromator with 1800 lines/mm, an emission monochromator with 600 lines/mm, and a liquid nitrogen cooled Hamamatsu R5509-72 near-infrared photomultiplier tube. For the lifetime measurements, the setup includes a Nd:YAG laser, equipped with second, third, and fourth harmonic options (allowing laser excitation at 532, 355, and 266 nm, respectively). The repetition rate is 10 Hz, and the pulse width is 3−5 ns.

Chemicals. Hydrated lanthanide chloride and nitrate salts (99.9%) were purchased from Aldrich, Acros Organics, or GFS Chemicals, and were used as received. The ligands were purchased from Acros Organics, except 5,7-diiodo-8-quinolinol (Aldrich), and recrystallized several times in chloroform and ethanol. Sodium hydroxide (Applichem, pellets), ammonium acetate (Acros, pa), and ammonium hydroxide solution (Ashland Chemical, 30%) were used as received. Ethanol (Fisher Scientific, absolute), methanol (Applichem, for synthesis), and acetone (Acros organics, pa) were used without further drying. The DMSO (Fisher, analytical-grade reagent) and dioxane and chloroform (Acros, pa) for the spectroscopic measurements were also used without further treatment.

Synthesis. The following syntheses were carried out for all the ligands in Scheme 1 except when mentioned otherwise. The rare-earth ions used are yttrium(III), erbium(III), and ytterbium(III). For each synthesis, one or two typical examples will be given. Typically, diamagnetic yttrium(III) complexes will be discussed, because they could be easily analyzed by ^{1}H NMR as well. The NMR data of samples containing trimer complex are available as Supporting Information, in which a full 2D COSY and NOESY NMR study of the trimeric species is present. A full list of elemental analysis data is available as Supporting Information as well, for every complex studied in the framework of this investigation (Table S3). The synthetic methods that have been used without modification to their literature description are referred to by method A, B, or C. The modified procedures are referred to by either the type of method

(A, B, or C), followed by "altered", or the type of complex that results from this procedure (e.g., tetrakis).

Method A. This method was used as described.[27] Using the ligands without a substituent in the 7-position results in a mixture of trimer (main product), tetrakis, and a marginal fraction of a third yet undefined product. The other ligands give a mixture of tetrakis, free ligand, and mainly tris. (YQ) MS: m/z 1418.9 ($Y_3Q_8^+$) (in CH_2Cl_2/CH_3OH). CHN Found: C, 59.28; H, 3.62; N, 7.52. Calcd as trimer $Y_3C_{72}H_{48}N_9O_{11}$: C, 58.35; H, 3.26; N, 8.51. (YQ57Cl) MS: m/z 764.2 ($Y(Q57Cl)_3(H_2O)_2$) and 940.9 ($Y(Q57Cl)_4^-$) (in CH_3CN). CHN Found: C, 43.52; H, 2.30; N, 5.47. Calcd as tris $YC_{27}H_{16}Cl_6N_3O_5$: C, 42.44; H, 2.11; N, 5.50. NMR (300 MHz, δ, DMSO): (tris $Y(Q57Cl)_3(H_2O)_2$) 8.94 (d, H_2), 8.37 (d, H_4), 7.62 (q, H_3), 7.58 (s, H_6); (tetrakis $NH_4[Y(Q57Cl)_4]$) 9.16 (d, H_2), 8.31 (d, H_4), 7.67 (q, H_3), 7.46 (s, H_6); ratio tris/tetrakis 2/1.

Method A Altered. The ligand (HQ, HQ5Cl, and HQ57Cl) (0.0016 mol) was dissolved in ethanol (50 mL) and slowly added to the erbium(III) chloride (0.0005 mol) in ethanol (100 mL). Afterward 10 drops of ammonium hydroxide solution were added. The solvent was partially removed after 10 min, and the remaining residue was filtered. The precipitate was washed with hot water and dried at 110 °C during the night. This synthesis gives the same kind of mixtures as the previous one. (ErQ) MS: m/z 1654.1 ($Er_3Q_8^+$) (in CH_2Cl_2/CH_3OH). CHN found: C, 50.77; H, 3.10; N, 6.25. Calcd as trimer $Er_3C_{72}H_{57}ClN_9O_{11}$: C, 49.09; H, 3.26; N, 7.16. Calcd as tetrakis $ErC_{36}H_{28}N_5O_4·H_2O$: C, 56.75; H, 3.44; N, 7.35. (ErQ57Cl) MS: m/z 1019.8 ($Er(Q57Cl)_4^-$), 1642.2 (br) ([Er-$(Q57Cl)_3]_2$). CHN Found: C, 38.80; H, 2.19; N, 5.17. Calcd as tris $ErC_{27}H_{16}Cl_6N_3O_5$: C, 38.36; H, 2.27; N, 4.97.

Method B. This method was used as described only for 8-hydroxyquinoline.[47] This method gives virtually pure trimer. (YQ) CHN Found: C, 57.46; H, 3.45; N, 7.21. Calcd as trimer $Er_3C_{72}H_{54}ClN_8O_{11}$: C, 57.29; H, 3.61; N, 7.42.

Method C. This method was used as described.[25] When HQ and HQ5Cl are used in this way, the resulting mixture contains mainly trimer. On the other hand, the 7-substituted ligands give a mixture of free ligand, tris, and mainly tetrakis. (YQ) MS: m/z 1418.9 ($Y_3Q_8^+$) (in CH_2Cl_2/CH_3OH). CHN Found: C, 57.59; H, 3.31; N, 6.94. Calcd as trimer $Y_3C_{80}H_{57}N_8O_{13}$: C, 57.98; H, 3.75; N, 7.31. (YQ57Cl) MS: m/z 940.8 ($Y(Q57Cl)_4^-$) (in CH_3CN). CHN Found: C, 44.38; H, 2.20; N, 6.50. Calcd as tetrakis $YC_{36}H_{22}Cl_8N_9O_5$: C, 44.25; H, 2.27; N, 7.17. NMR (300 MHz, δ, DMSO): (tris $Y(Q57Cl)_3(H_2O)_2$) 8.94 (d, H_2), 8.37 (d, H_4), 7.63 (q, H_3), 7.60 (s, H_6); (tetrakis $NH_4[Y(Q57Cl)_4]$) 9.16 (d, H_2), 8.33 (d, H_4), 7.63 (q, H_3), 7.48 (s, H_6); ratio tris/tetrakis 1/4.

Tetrakis. The sodium salt of the ligand (HQ, HQ5Cl, HQCl57) was prepared in solution by adding NaOH (0.0012 mol) to the ligand (0.0012 mol) in ethanol (100 mL) at 70 °C. After 30 min the rare-earth chloride (0.0003 mol) dissolved in ethanol (50 mL) was slowly added. The resulting solution was stirred overnight at 70 °C. The precipitate was filtered and washed with water and ethanol. The resulting complex was dried at 110 °C overnight. The dried precipitate is a pure tetrakis complex with a sodium counterion. (YQ57Cl) MS: m/z 938.9 ($Y(Q57Cl)_4^-$) (in CH_3CN). CHN Found: C, 44.28; H, 1.48; N, 5.45. Calcd as tetrakis $YNaC_{72}H_{16}Cl_8N_4O_4·^1/_2H_2O$: C, 44.44; H, 1.76; N, 5.76. NMR (300 MHz, δ, DMSO): ($Na[Y(Q57Cl)_4]$) 9.16 (d, H_2), 8.33 (d, H_4), 7.63 (q, H_3), 7.48 (s, H_6).

Tris. HQ57Cl (0.0019 mol) was dissolved in dichloromethane (50 mL). This solution was stirred at room temperature with a solution (40 mL) of the rare-earth chloride (0.0008 mol) and ammonium hydroxide (0.0008 mol) in water. After one night the resulting precipitate was filtered and dried at 110 °C. It contained

75% of the tris complex. (YQ57Cl) CHN Found: C, 43.68; H, 1.82; N, 5.13. Calcd as tris $YC_{27}H_{16}Cl_6N_3O_5$: C, 43.47; H, 1.89; N, 5.63. NMR (300 MHz, δ, DMSO): (tris $Y(Q57Cl)_3(H_2O)_2$) 8.94 (d, H_2), 8.37 (d, H_4), 7.62 (q, H_3), 7.60 (s, H_6); (tetrakis NH_4-$[Y(Q57Cl)_4]$) 9.16 (d, H_2), 8.31 (d, H_4), 7.63 (q, H_3), 7.47 (s, H_6); ratio tris/tetrakis 5/1.

Crystallography. Crystals of compounds **2** and **7**, suitable for X-ray diffraction, were obtained by slow evaporation from dioxane at room temperature. Compound **4** crystallized by slow evaporation from $CHCl_3$ at 4 °C, and compound **5** crystallized by dioxane/EtOH two-phase diffusion at room temperature. All crystals had a yellow color. Crystals were mounted in a nylon loop for data collection at 100 K on a SMART 6000 diffractometer equipped with a CCD detector using Cu Kα radiation ($\lambda = 1.54178$ Å). The images were interpreted and integrated with the program SAINT from Bruker.[53] The four structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[54] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at $1.2U$(eq) of the parent atoms.

(53) *SAINT*, Manual Version 5/6.0; Bruker Analytical X-ray Systems Inc.: Madison, WI, 1997.
(54) *SHELXTL-NT*, Manual Version 5.1; Bruker Analytical X-ray Systems Inc.: Madison, WI, 1997.

Supporting Information Available: Additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC-256492, CCDC-256493, CCDC-256494, and CCDC-256495 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, U.K.; fax +44−1223−336033 or e-mail deposit@ccdc.cam.uk).

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