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Review

8-Hydroxyquinolines in metallosupramolecular chemistry

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Contents

Abstract

8-Hydroxyquinoline is a versatile ligand in coordination chemistry which was mainly used for analytical purposes. Due to the special properties of some of its complexes it experienced a renaissance in synthetic coordination chemistry. This review describes recent applications of 8-hydroxyquinoline derivatives to obtain new supramolecular sensors, emitting devices or self-assembled aggregates.

Keywords: 8-Hydroxyquinoline; Luminescence; Sensor; Self-assembly; Helicate

1. Introduction

Supramolecular chemistry is loosely defined as the “chemistry beyond the molecule” or the “chemistry of non-covalent interactions” [1]. Both expressions illustrate that it focuses on aggregation of molecular building blocks, which attract each other by formation of non-covalent bonds (e.g. van der Waals, electrostatic, hydrogen bonding, etc.). Favourable interactions between complementary molecules occur in *molecular recognition processes* following Emil Fischers key-and-lock principle [2]. This leads to the specific aggregation of well-defined supramolecular structures by *self-assembly* of two or more components. The reversibility of non-covalent interactions allows an error correction during the assembly process. Although the formation and the geometries of the final architectures are already of interest, it is furthermore important to investigate and understand the special properties – the *supramolecular function* – of the whole ensemble in comparison to the isolated building blocks [3].

The bond between metals and ligands possesses a high degree of covalency in addition to dipole–dipole or electrostatic attractions. Nevertheless, metal–ligand interactions are very often dynamic, meaning that they can reversibly be formed and broken. Therefore they are also used to obtain supramolecular aggregates. This field of research is termed *metallosupramolecular chemistry* [4]. Using metals and ligands with specific geometries, it is possible to make impressively large oligonuclear coordination compounds and to use self-assembled metallosupramolecular containers for the inclusion of reactive intermediates or to support (or catalyse) chemical reactions within the cavities of the assemblies [5].

Pyridine derivatives, either as the parent units or as higher oligomers (bipyridine, terpyridine, etc.), are very often used as

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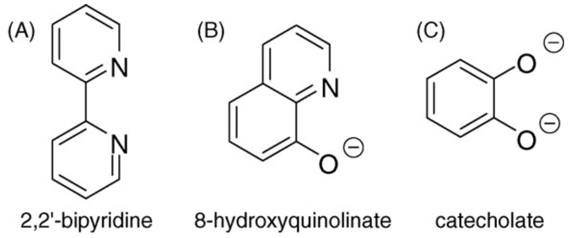


Fig. 1. Comparison of the chelating units of bipyridine, 8-hydroxyquinolinate, and catecholate.

appropriate building blocks to be incorporated in ligands [6]. Especially 2,2′-bipyridine **A** (bipy) is frequently found, because it forms highly stable entities with metal ions [7]. In contrast to the neutral bipyridine **A**, catecholate ligands **C** possess a charge of 2− and therefore address another kind of metal ions. The latter ligand unit recently has been intensely studied [8]. In this review the coordination and supramolecular chemistry of the 8-hydroxyquinoline moiety **B** will be described. It can be considered as a hybrid in between the two coordinating sites **A** and **C**. On the one hand, hydroxyquinolinate possesses one pyridine donor of bipy and one phenolate unit of catecholate. Therefore (in its deprotonated form) it is monoanionic and bridges the gap between the neutral bipyridine and the dianionic catecholate. On the other hand, the geometry and chelating size of **B** are the same as found for **A** and **C** (Fig. 1).

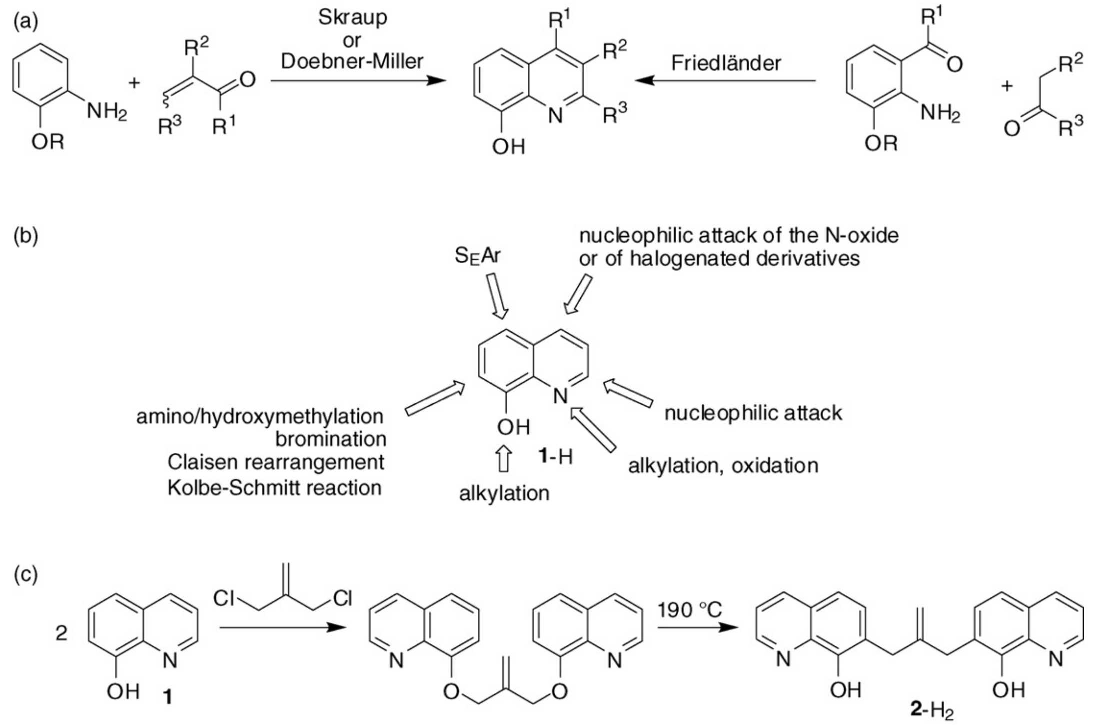
Initially the 8-hydroxyquinoline ligand has been mainly applied for analytical purposes and separation techniques. Due to the extraordinary coordinating abilities this ligand is an excellent reagent for gravimetrical analysis and it can be used for the extraction of metal ions [9]. More recently 8-hydroxyquinoline became an interesting chelating agent for the formation of luminescent coordination compounds either for light emitting devices [10] or in sensors and diagnostics (e.g. in bioconjugates) [11]. Clioquinol (5-chloro-8-hydroxy-7-iodoquinoline) is on the market as a highly potent antisepticum [12]. The compound is an effective copper(II) and zinc(II) chelator and inhibits the ubiquitination and asparagine hydroxylation of the hypoxia-inducible factor-1α (HIF-1α), leading to an expression of its target genes [13].

The 8-hydroxyquinoline unit is an ideal building block in metallosupramolecular chemistry. Its special coordinating features are important for the *molecular recognition* of metal ions, which in appropriate derivatives can induce the *self-assembly* of specific oligomeric complexes with certain emitting properties and the corresponding *supramolecular functions*.

2. Synthetic and structural aspects of 8-hydroxyquinoline derivatives

8-Hydroxyquinoline and its derivatives are generally prepared by the Skraup [14] (or Doebner–Miller [15]) or the Friedländer [16] syntheses. An elegant protocol for the Skraup synthesis was developed by O'Murchu using NaI as a catalyst for the cyclization to obtain high yields of the quinoline [17].

Substituents at the quinoline unit can be introduced either during the preparation of the bicycle (as it is indicated in Scheme 1a) or by modifications at various positions of the parent system **1**-H. The hydroxide can be easily alkylated or acylated, allowing the introduction of appropriate protecting groups. The nitrogen atom can be protonated, alkylated or oxidized in order to modify



Scheme 1. Preparation of 8-hydroxyquinoline derivatives (a) and possible functionalizations at the 8-hydroxyquinoline skeleton (b). As a representative example the formation of an isobutenylidene-bridged bis-8-hydroxyquinoline by the Hiratani-tandem-Claisen rearrangement is shown (c).

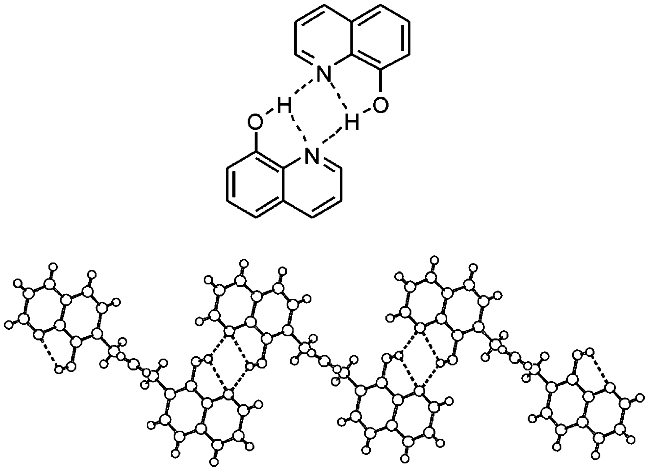


Fig. 2. Hydrogen bonding pattern in dimeric 8-hydroxyquinolines and the solid state structure of the hydrogen bonded polymer of **2**-H_2.

the reactivity at the pyridine unit. This is important for the activation of the 2- or the 4-position for attack of nucleophiles. The 5- and 7-positions can be functionalized by electrophilic aromatic substitutions with a special emphasis on amino- and hydroxyalkylation or Kolbe–Schmitt reaction to specifically address the 7-position. Claisen rearrangement introduces an allyl substituent in the latter position [18].

The simple preparation of a bis-hydroxyquinoline derivative **2**-H_2 by Williamson ether synthesis of **1**-H with 3,3′-dichloroisobutene followed by Hiratani-tandem-Claisen rearrangement is shown as a representative example in Scheme 1c. The rearrangement reaction proceeds quantitatively within minutes at 190 °C [19].

In the solid phase 8-hydroxyquinolines tend to dimerize by formation of bifurcated hydrogen bonds as it is indicated in Fig. 2. In the case of alkyl-bridged bis-8-hydroxyquinolines (e.g. **2**-H_2) this leads to polymerization upon crystallization [20]. Hereby, the conformation of the polymer can be influenced by introduction of spacers with either odd or with even numbers of carbon atoms in the bridge. With an odd number, the polymer adopts a zigzag conformation while with an even number, a polymer with a double-wound “8”-type structure is observed. The structural influence of this “even–odd” principle on metal coordination will be described later on in the context of “helicate stereochemistry” (vide infra).

3. Coordination compounds of 8-hydroxyquinoline derivatives

In this article the supramolecular coordination chemistry of 8-hydroxyquinoline derivatives will be in the focus of attention. This means that molecular recognition and self-assembly processes as well as host–guest systems will be discussed. However, selected simple Werner-type complexes will be also included to illustrate the special properties of quinolinates. They are important for the preparation of functional metallosupramolecular materials.

3.1. O-Alkylated quinolinates as ligands

As far ago as the 1970s quinolinate-substituted podand-type ligands were applied for the selective complexation of various metal ions. The use of ether linked quinolines, like the derivatives **3**, for the recognition of e.g. alkaline metal cations and the thereby formed structures were thoroughly reviewed early on by Vögtle and Weber [21].

Just recently this kind of ligand has experienced a renaissance. For example, compounds **4** and **5** were reacted with silver(I) ions. Both of the ligands form coordination compounds, in which they bridge two strongly distorted tetracoordinated metal centers that in addition bind another one of the ligands. This leads, e.g. to the trinuclear circular compound $[\{Ag(\mathbf{4})\}_3]^{3+}$ with three ligands wrapping helically around a triangle of silver cations (see Fig. 3). Structures of this kind are termed *circular helicates* [22]. Ligand **5** yields a linear polymeric structure $[\{Ag(\mathbf{5})\}_n]^{n+}$ with alternating configuration at the metal complex units [23].

In addition to double quinolinate-substituted ethers, tripodal or tetrapodal derivatives like **6a**,**b** were also prepared and their ability to bind silver cations (and also Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, or Cd^{2+}) was studied by fluorescence measurements [24].

3.2. Visible and NIR emitting complexes

Trisquinolinate aluminum is a standard emitter for the preparation of light emitting diodes [25]. In its parent form it usually shows electroluminescence in the green region (approximately 525 nm) [26]. Due to this property, aluminum quinoline derivatives **7** and **8** were extensively studied (Fig. 4).

It has been reported, that the facial and the meridional isomers of aluminum quinolinate can be selectively prepared by applying different reaction conditions. Surprisingly the thermodynamically less favoured facial isomer **7** (fac) is obtained from **7** (mer) by prolonged heating in deionized water [27]. Usually the facial isomer is the desired one due to its special photophysical properties [28].

Substitution at the 5-position of the quinoline changes the electronic situation [29]. If methyl substituents are introduced at the 2-positions of the quinolines, the complex gets sterically crowded and only two of the ligands are bound to aluminum(III). Phenolate can act as a coligand (**8**) and enables a fine tuning of the photophysical properties by additional substituent effects [30].

Zinc(II) complexes of quinolinate derivatives also show interesting luminescent and electroluminescent properties, which are less ionic and thus are different to the aluminum complexes (Fig. 5). Because of the ability of the zinc(II) cation to adopt a broad scope of different coordination geometries and numbers, the structures are very versatile.

For example, with the simple 8-hydroxyquinoline ligand **1**-H the mononuclear complex **9** is obtained. It contains two quinolinates and two molecules of water as coligands [31]. Synthesis of the compounds under anhydrous conditions affords the tetramer **10**. The latter has been used to prepare electroluminescent devices by vapour deposition techniques and shows special

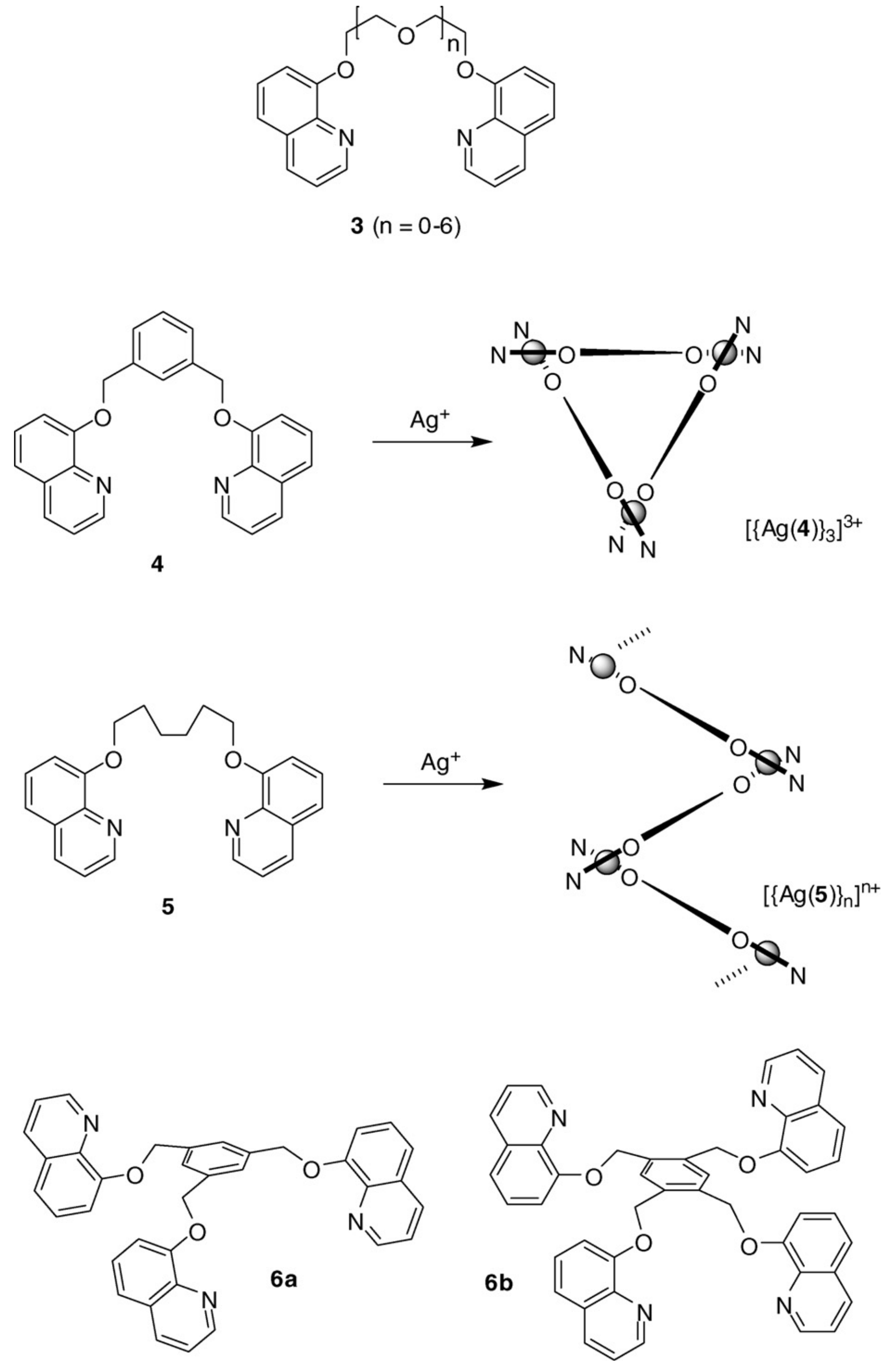


Fig. 3. Quinolinate ether ligands **3**–**6**, which are used for the recognition of alkali metals (**3**) or silver ions (**6**). Ligand **4** forms a trinuclear circular helicate $[\{\mathrm{Ag}(\mathbf{4})\}_3]^{3+}$, and **5** a polymer $[\{\mathrm{Ag}(\mathbf{5})\}_n]^{n+}$ (only schematic representations of the coordination compounds are shown).

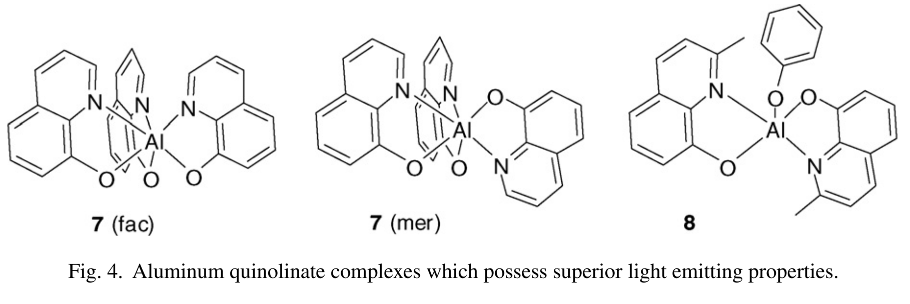


Fig. 4. Aluminum quinolinate complexes which possess superior light emitting properties.

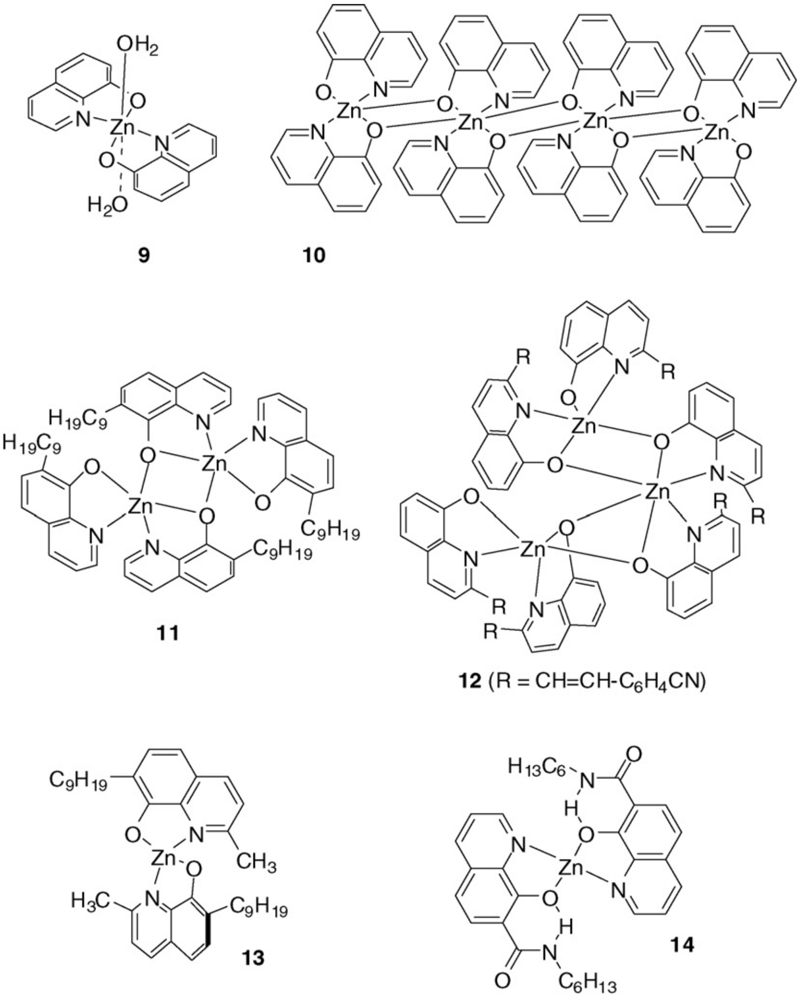


Fig. 5. Zinc(II) complexes with monotopic 8-hydroxyquinoline-derived ligands.

electron transport properties because of the π–π stacking of the coordinated ligands in the crystal [32].

The complexes **11** and **12** represent compounds containing quinolinates which are monosubstituted, either in 7- or in 2-position. **11** adopts a dimeric structure with phenolate bridging [33], while in **12** a similar aggregation results in a trimer. The substitution of **12** causes an emission in the red [34].

Attachment of alkyl groups in 2- as well as in 7-position of the quinolinate leads to some steric bulk, which enforces a pseudo-tetrahedral coordination at zinc(II) as it is found in **13** [33]. In **14** the quinolinate ligand is amide substituted, and a 1:2 complex is formed which shows intramolecular hydrogen bonding between the amide NH and the quinolinate oxygen. In the solid state **14** polymerizes by binding of a carbonyl of one complex unit to the zinc of the next leading to an effective five-fold coordination at the metal [35].

The photophysical properties of the quinolinate complexes with aluminum and zinc ions are determined by electronic transitions at the coordinated ligand. The metal mainly influences on favouring the intersystem crossing between the singlet and triplet excited states at the ligand.

The combination of quinoline derivatives with rare earth elements, which have the potential to luminesce should also lead to interesting compounds. However, due to the low lying excited states at the quinoline, an effective energy transfer to the lanthanide center can only take place with the NIR emitters erbium(III), neodymium(III), and ytterbium(III). Hereby most studies focus on erbium(III) and it has been shown that the NIR emission of quinolinate complexes of this metal with the general composition of 3:1 can be enhanced by attaching heavy atoms (chloride or bromide) to the ligand [36].

Structural investigations show that different complexes are formed by coordination of quinolinates to erbium(III). However, the formation of the certain species can be controlled by the method of preparation.

Compounds **15a** and **15b** represent related trinuclear complexes. Two tetraquinolinate erbium units coordinate as tridentate ligands through bridging phenolate oxygen atoms to a central erbium atom which additionally bears either a quinolinate [37] or an acetate. A further trinuclear complex is the cation **16**. Two terminal trisquinolinates (which coordinate either one water or one hydroxide as coligand) bind to a central bisquinolinate erbium unit with all the quinolinate oxygen atoms involved in the connection of the units (Fig. 6).

Mononuclear erbium compounds with four or three quinolinate ligands are present in **17** and **18**, respectively. **18** is a rare

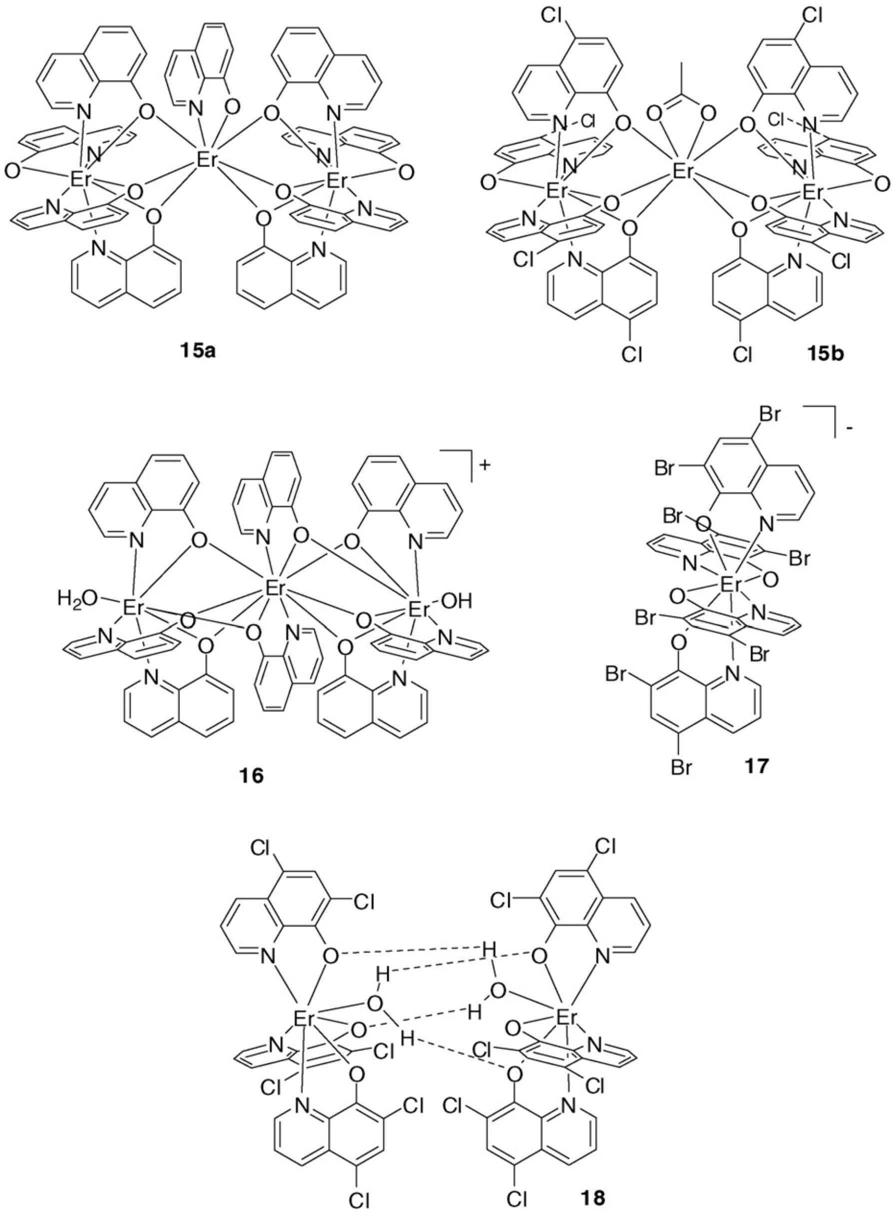


Fig. 6. Structures which were observed for bidentate quinolinate ligands with erbium(III) ions.

structural example (vide infra) in which only three quinolinates coordinate to the rare earth ion. Water acts as coligand and leads to dimerization of the compound by hydrogen bonding in the crystal [38].

In order to control structural as well as photophysical properties of the complexes, it is desirable to prepare well-defined mononuclear complexes in which the central metal is shielded from solvent molecules. A reasonable approach towards this goal is to extend the coordination site of 8-hydroxyquinoline via attaching additional donor moieties.

The hydrazone derivatives **19a**-H and **19b**-H usually act as tetradentate ligands and form 1:1 (or in few occasions 2:1) complexes. In the solid phase very often dimerization by anion bridging is observed [39].

Amide-substituted ligands **20**-H, on the other hand, are ideal to form nonacoordinated rare earth complexes and thus effectively shield the central metal against the penetration of water into the first coordination sphere. This is shown in Fig. 7 in form of the X-ray structures of *syn*-[Er(**20a**)$_3$] and *anti*-[Yb(**20c**)$_3$]. In the solid phase, the compounds exhibit NIR emission, which can be successively enhanced by the respective substitution of one or two hydrogen atoms at the quinoline by bromine (**20a** → **20b** → **20c**) [40].

3.3. Crown ether–8-hydroxyquinoline conjugates

The coordination ability of the 8-hydroxyquinoline unit has been combined with the feature of crown ethers to specifically recognize metal cations by means of introducing macrocycles in the backbone. The advantage of such a conjugate is the property of the quinolinate moiety to act as a fluorophoric metal ion sensor [41]. A whole series of ligands has been designed and

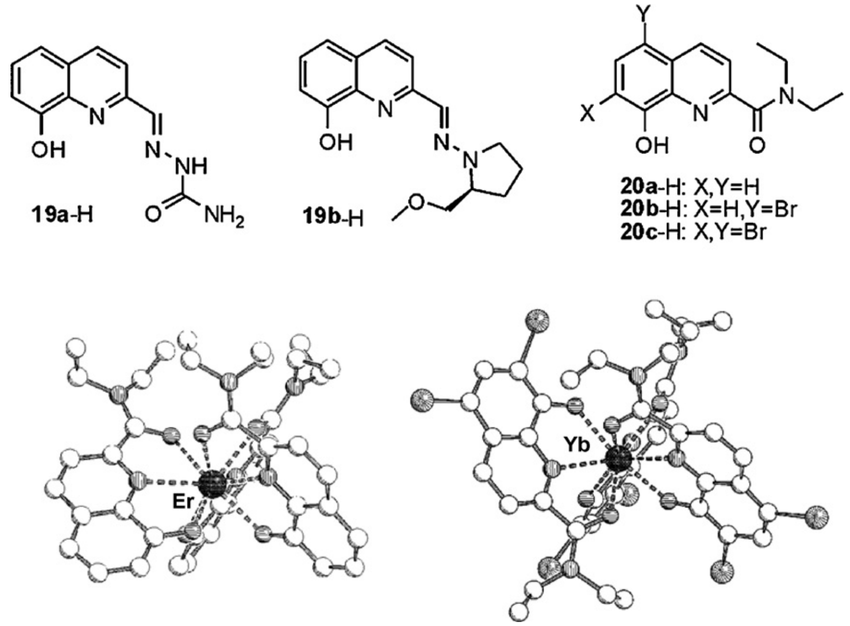


Fig. 7. Expanded 8-hydroxyquinoline coordination sites and the solid phase structures of *syn*-[Er(**20a**)$_3$] and *anti*-[Yb(**20c**)$_3$].

investigated as new sensing materials [42]. The most intensively studied compounds **21**-H_2 and **22**-H_2 possess two chloroquinolinate units. They are depicted in Fig. 8. Upon addition of metal ions, different coordination modes occur, which have an influence on the selectivity of the binding and on the photophysical properties of the formed complexes. After inclusion of a metal ion in the crown ether, both quinolinate units can bind to the metal either from the same or from opposite sides of the ring. As an alternative, only one quinolinate coordinates to the metal, while the second quinolinate is dangling around without coordination. Respective X-ray structures have been observed for free ligands as well as for barium complexes [43]. With zinc(II) or mercury(II) related compounds are found, in which the metals are not bound by the crown ether but only by the quinolinates [44].

The ligand **22a**-H_2 can be used as a sensor for magnesium ions. The macrocycle fluoresces in the presence of Mg^{2+} but not with other alkaline earth ions. The high sensitivity of **22a** for magnesium and the strong response by fluorescence enable the use of this compound for the detection of the divalent ion under strongly competing conditions. It even is possible to sense magnesium within living cells. This has been used to map intracellular ion distribution and movement [45].

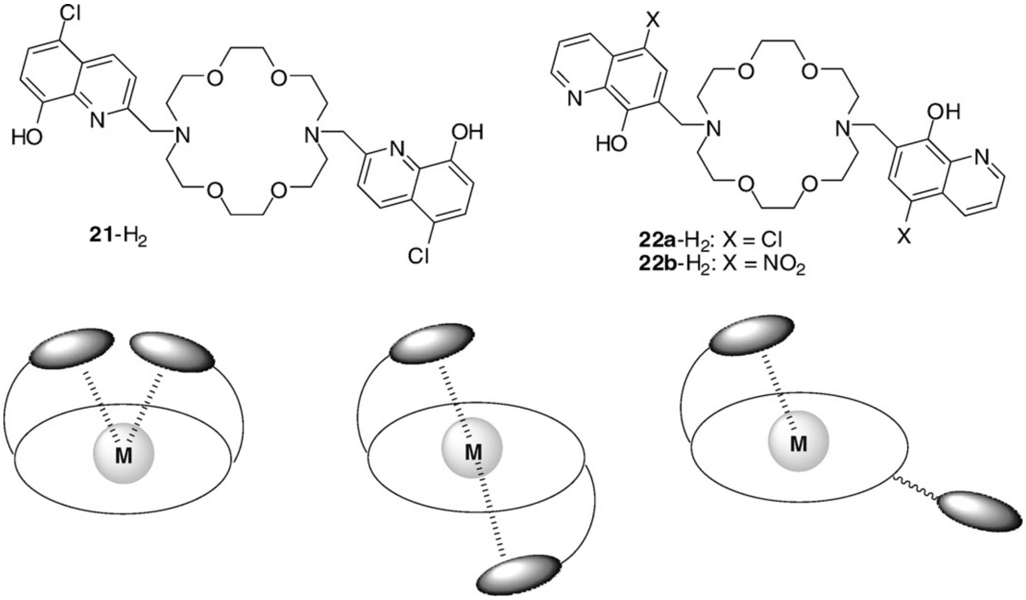


Fig. 8. Quinolinate–crown ether conjugates which were frequently used as sensors for metal ions.

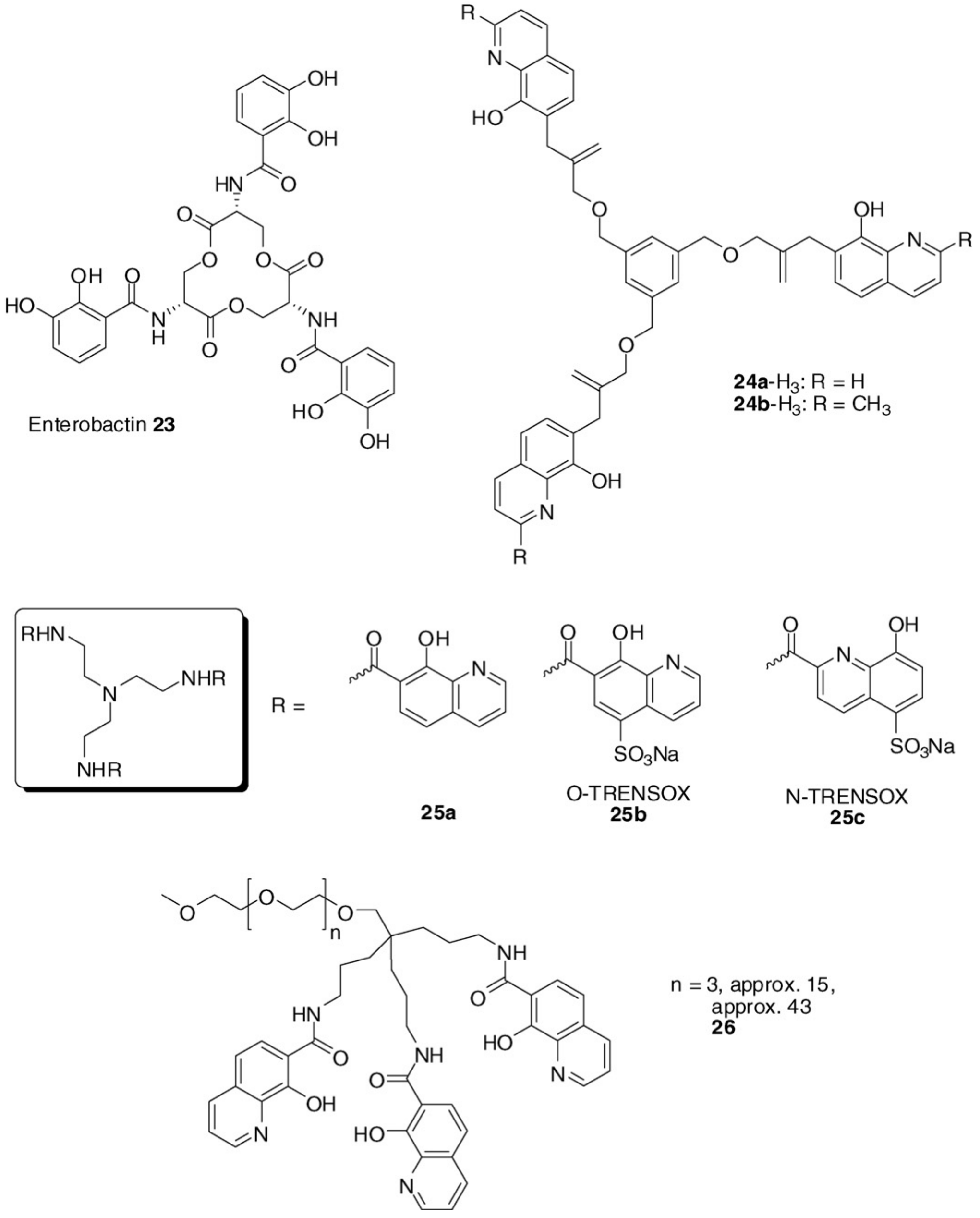


Fig. 9. Tripodal ligands for the sequestering of metal cations.

The corresponding nitro derivative **22b**-H$_2$ proved to be a highly selective sensor for mercury(II) ions. It displays a good affinity and selectivity for this ion over a range of >2 pH units [46].

3.4. *Complexes with tri- and tetrapodal ligands*

Enterobactin **23** is a naturally occurring Siderophore which contains three catechol amide units connected to a macrocyclic tris-serinolactone. The chirality of the backbone leads to an ideal orientation of the catechol units for the binding of "hard" metal ions. One of the highest binding constants is found with iron(III) ions [47].

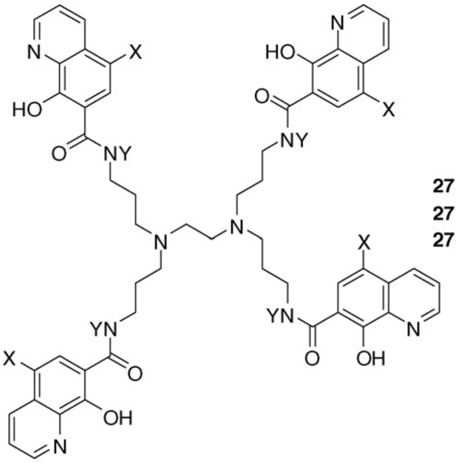
Enterobactin **23** has been inspiring to develop artificial tripodal ligand systems for the specific binding of metal ions with high affinities. Fig. 9 presents some tripodal 8-hydroxyquinolinate ligands, which in their design follow this concept.

Hiratani et al. describe tripodal "Enterobactin analogues" **24a**,**b**-H$_3$ that bear 8-hydroxyquinoline units as chelating sites. The ligands are prepared by a tandem-Claisen rearrangement reaction. Jobs plot analysis shows the formation of 1:1 complexes of **24b** with iron(III) or gallium(III). At low pH (<4) selectivity for the gallium(III) ion is found, which is high against Al^{3+}, In^{3+}, or La^{3+} and moderate against Fe^{3+} [48].

Many tripodal tris-8-hydroxyquinoline derivatives have been constructed based on the tren (tri(aminoethyl)amine) backbone and on amide linkages. As representative examples the compounds **25** are shown in Fig. 9. In order to introduce high water solubility, sulfonate groups are attached to the chelating units in compounds **25b** (O-TRENSOX) and **25c** (N-TRENSOX). Both ligands prove to be potent iron chelators (iron(II) as well as iron(III)). The iron(III) complex of O-TRENSOX has been shown to prevent and reverse iron chlorosis in several plant species. In experiments with rat hepatocyte cultures it has been found out, that O-TRENSOX is effective in the decrease of iron uptake as well as in the increase of iron release by the cells. Equilibrium constants for the binding of iron(III) to O- and N-TRENSOX have been determined. They show a stronger binding of the metal ion by O-TRENSOX in comparison to N-TRENSOX. The affinity of different metal ions to O-TRENSOX results in a series Fe^{3+} (pM = 29.5), Cu^{2+} (22.9), Zn^{2+} (21.7), Al^{3+} (20.0), Fe^{2+} (17.4), and Ca^{2+} (13.6) [49].

The ligands **26** provide an iron(III) binding ability, which is similar to the one of O-TRENSOX. However, the complexes of **26** possess a well-balanced hydrophilicity/hydrophobicity that makes them interesting phase transfer reagents and membrane transporters [50].

In recent studies a series of ligands has been prepared, which are related to the TRENSOX family, but contain 8-hydroxyquinoline as well as catechol binding sites for metal ions [51].



27a: X,Y = H
27b: X = SO_3^-, Y = H
27c: X = SO_3^-, Y = CH_3

Fig. 10. Tetrapodal hydroxyquinoline ligands for the coordination of rare earth ions.

The tetrapodal ligands **27** have been developed based on the results obtained with the TRENSOX ligands (Fig. 10). The coordination sites are designed in such a way that they are appropriate to bind large rare earth ions and to satisfy their coordination requirements. Starting with **27a**, sulfonation affords the water soluble derivative **27b**. Methyl groups at the amide are introduced in **27c** to avoid quenching of lanthanide emission by vibrational resonance of the NH units. Photophysical investigations show, that the ligands **27a** and **b** are good sensitizers for NIR emission of neodymium(III), erbium(III), and ytterbium(III) even in water solution [52]. Substitution of the amide NH by N-CH_3 in O-TRENSOX itself also affords good sensitizers for the NIR emission of neodymium(III), erbium(III), or ytterbium(III) in water. The latter complex couples to human serum albumin leading to an increase of the NIR luminescence by 50% [53].

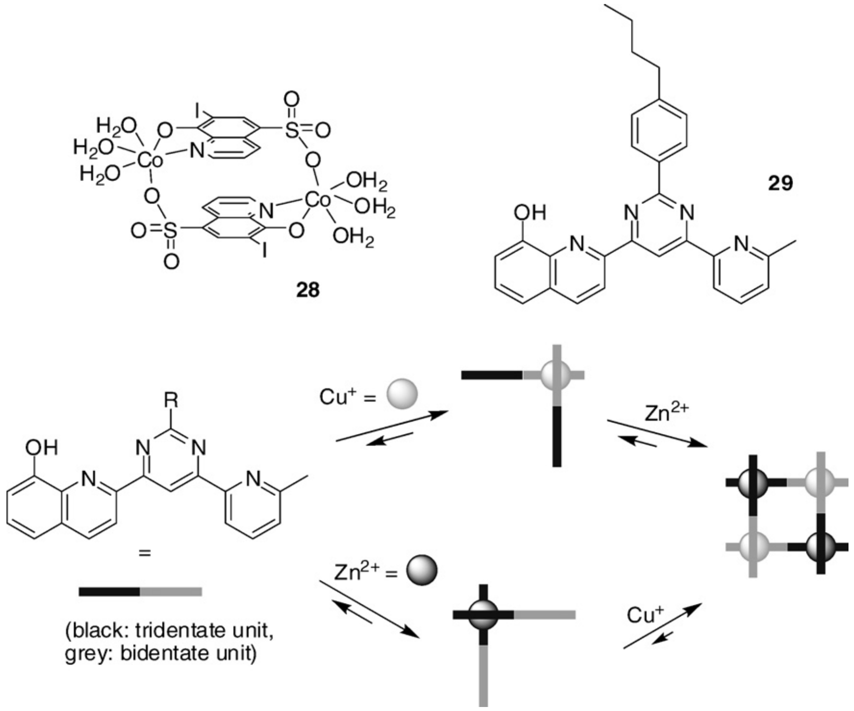


Fig. 11. Examples for self-assembled structures involving the 8-hydroxyquinoline binding site. A small square **28** and a heteronuclear [2 × 2] grid.

3.5. Self-assembly of oligonuclear coordination compounds

Ligands with two or more chelating units are used for the self-assembly of supramolecular architectures with grid-type, helical, tetrahedral, or even more complicated structures [54]. Despite its wide use in coordination chemistry 8-hydroxyquinoline played only a minor role in such investigations. Only in the last decade its potential in this field has been appreciated and first systematic studies have been done.

A small molecular square **28** self-assembles by mixing of ferron (8-hydroxy-7-iodo-quinolinyl-5-sulfonate) with cobalt(II) in the presence of water. The dimeric rectangular structure is stabilized by attractive π–π interactions between the two ferron ligands [55]. Similar π–π interactions have been used as the driving force for the inclusion of bis-quinolinato platinum(II) in macrocyclic cyclophane hosts in a 1:2 fashion [56].

Ligand **29** possesses two different binding sites with a pyrimidine unit being involved in both of them. The pyrimidine/pyridine moiety is bidentate, while a 2-pyrimidyl-substituted part is tridentate. Zinc(II) or lead(II) ions bind only to the tridentate unit forming a 2:1 complex in case of Zn^{2+} and a 1:1 complex with Pb^{2+}. The latter dimerizes in the crystal by triflate bridging. Copper(I), on the other hand, forms a 2:1 complex with the metal ions coordinating to the bidentate unit.

As it is indicated in Fig. 11, successive addition of either copper(I) followed by zinc(II) or zinc(II) followed by copper(I) yields initially the respective 2:1 complexes. After the second ion is added, a heterodinuclear molecular [2 × 2] grid is obtained, in which two zinc ions possess a pseudo-octahedral and two copper ions a pseudo-tetrahedral coordination geometry [57].

Alkyl-bridged bis-8-hydroxyquinoline derivatives **30**–**32**-H_2 and **2**-H_2 are versatile ligands to prepare dinuclear helicate-type coordination compounds in templated metal-directed self-assembly processes. Initially, the ethylene-bridged derivatives **31a**-H_2 and **31b**-H_2 were prepared [58]. The two ligands are very similar in geometry but are different in the orientation of

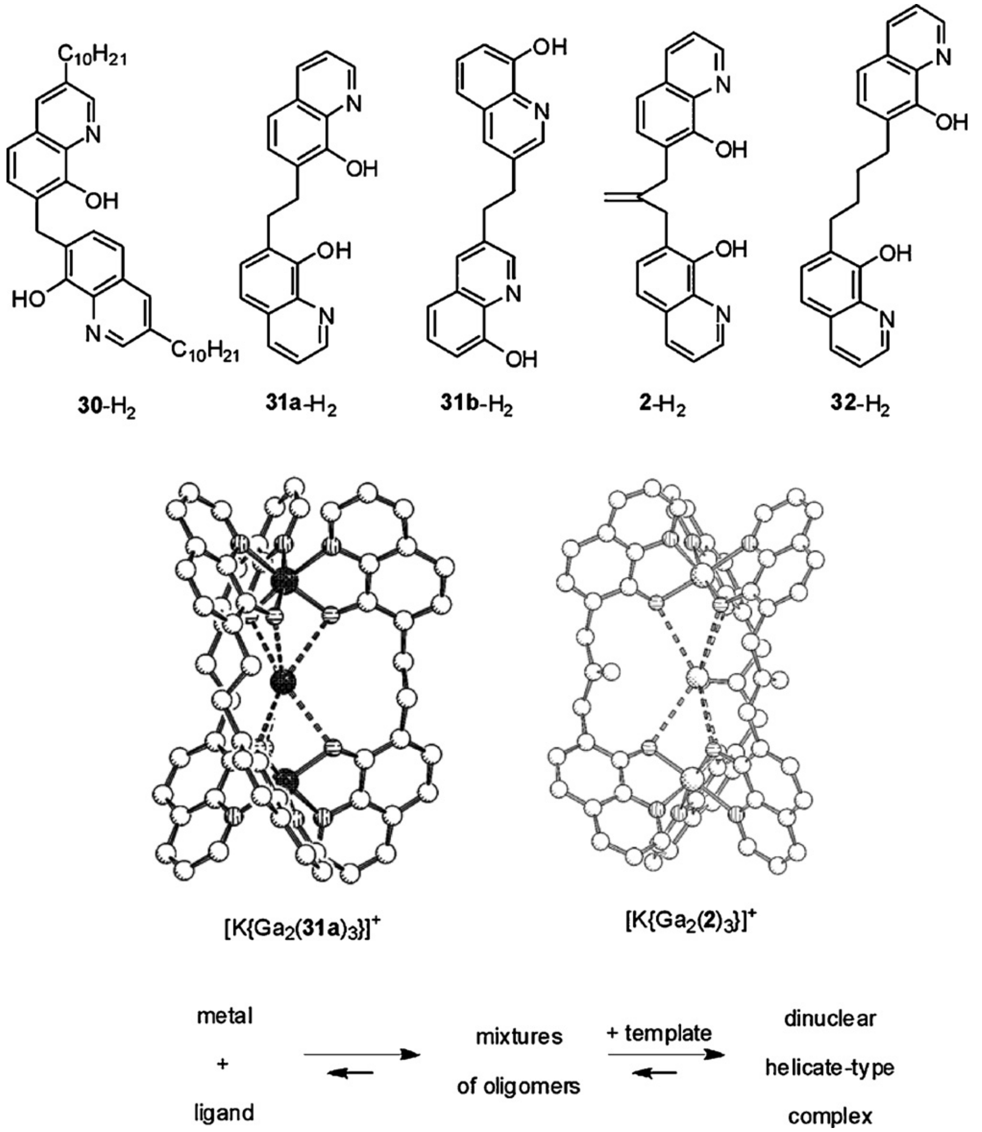


Fig. 12. Alkyl-bridged bis-8-hydroxyquinoline ligands (top) which are used in the template directed formation of dinuclear helicates or *meso*-helicates (centre) following the principle of “dynamic combinatorial chemistry” (bottom).

the donor atoms. **31a** possesses internal oxygen, **31b** internal nitrogen atoms. Upon coordination of a metal ion, the nitrogen atom will be "saturated" while oxygen still bears electron pairs which can be involved in the binding of another metal ion.

Reaction of the two ligands **31a**,**b**-H_2 with gallium(III) ions leads to the formation of insoluble material that by elemental analysis shows a composition of three ligands and two metals. If long alkyl chains are attached to the ligands, the material becomes soluble, but NMR spectroscopy reveals that no defined complex is present and a mixture of different "3:2" (ligand:metal) oligomers is found by MALDI TOF MS. If potassium or sodium salts are added to the mixtures of oligomers, they dissolve in case of ligand **31a** and a well-defined compound is observed by NMR. A part of the structure as found in the solid state is shown in Fig. 12 (centre left). Three ligands **31a** and two gallium(III) ions form a dinuclear triple-stranded helicate. In addition, one potassium cation is observed in the interior of this complex, coordinating to the internal oxygen atoms of the ligand. The latter is the reason for the different behaviour that is observed for the compounds with ligand **31a** compared to **31b**. Binding of potassium in the cavity of $[Ga_2(\mathbf{31a})_3]$ leads to a templating effect, which stabilizes the structure. In a dynamic process, this inclusion compound is quantitatively formed from the oligomeric material (dynamic combinatorial chemistry). In case of **31b** a similar templating is not possible due to the lack of internal oxygen atoms [59].

Related coordination studies were performed with the ligands **30**-H_2, **31a**-H_2, **2**-H_2, and **32**-H_2. Hereby different metals (gallium(III), aluminum(III), iron(III), chromium(III), or zinc(II)) were used and different cations (lithium, sodium, potassium, ammonium, rubidium, caesium) have been tested as templates. A strong dependence between the size of the template and the length of the spacer is found. Self-assembly of dinuclear helicates proceeds with the short ligand **30** only upon addition of the small templating lithium or sodium ions. Complexes of **31a** are formed with sodium, potassium, ammonium, and rubidium, while **2** accepts potassium, ammonium, rubidium, and caesium as templates. Helicate formation with **32** works only with the large caesium cation [60].

In addition to the templating, a stereocontrolling effect has been observed. The heterochiral *meso*-helicate (Fig. 12, centre right) is formed in case of ligands with an odd number of carbon atoms (**30**, **2**), while with an even number (**31a**, **32**) only the homochiral helicate (Fig. 12, centre left) is found. The reason for this is the preferred zigzag conformation of alkyl chains, which leads either to an orientation possessing a symmetry element of chirality (even: **31a**, **32**) or of non-chirality (odd: **30**, **2**). The concept to use the even–odd principle for stereocontrol in the formation of helicates or *meso*-helicates has already been introduced earlier for catecholate complexes [61].

Coordination of a heteroditopic ethylene-bridged catechol/8-hydroxyquinoline ligand to gallium(III) ions results in the formation of a dinuclear compound with two ligands directed in one direction and the third in the opposite one [62]. The control of the ligand orientation is due to the minimization of charge separation between the two metal complex units in the dinuclear coordination compound [63].

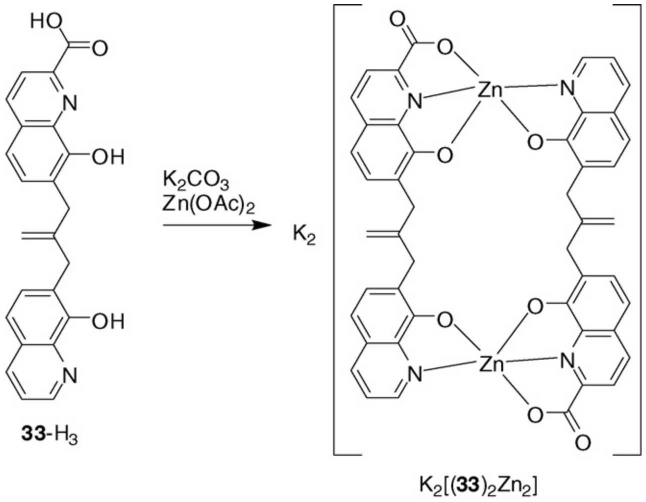


Fig. 13. A sequential quinolinate ligand **33**-H_3 and its dinuclear zinc(II) complex with an anti-parallel orientation of the ligands.

33-H_3 represents a heterobidentate ligand with bi- and tridentate quinolinate units. This ligand forms a dinuclear complex $[Zn_2(\mathbf{33})_2]^{2-}$, in which the two ligands are oriented in an anti-parallel fashion leading to pentacoordination at each zinc(II) ion [64] (Fig. 13).

In the helicates, two metal complex moieties are connected by spacers, each bridging two ligands of the respective metal complex units. Introducing non-covalent connections in the spacer allows hierarchical assembly of the helicates. In the first step, mononuclear complex units are obtained, which in the second step aggregate into dinuclear complexes. This is demonstrated in Fig. 14 for the formation of dinuclear nickel(II), cobalt(II), or zinc(II) complexes, which are held together by three lithium cations.

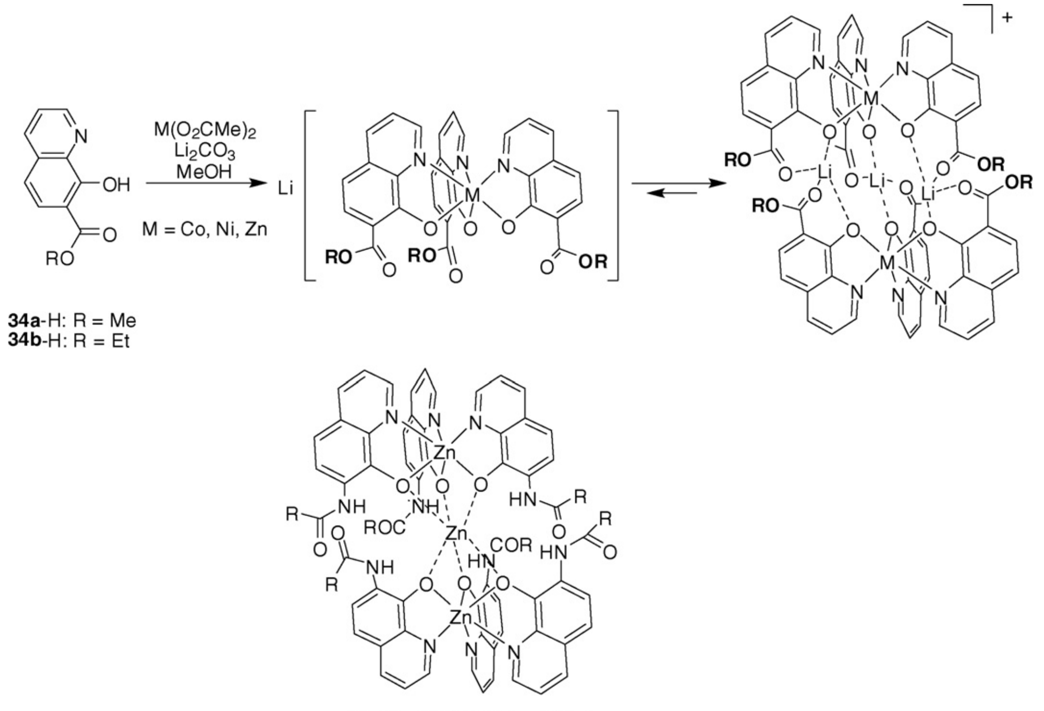
The hierarchical assembly proceeds in this case due to two different binding sites at the ligands **34**, the hydroxyquinoline for the coordination of the transition metal cations and the salicylate for lithium. However, coordination of the lithium to the salicylate is not sufficient to obtain the dimer. Additional electrostatic attraction by negatively charged monomeric trisquinolinate complex units is necessary. In case of neutral coordination compounds $Al(\mathbf{34})_3$ or $Ga(\mathbf{34})_3$ no dimerization takes place in the presence of lithium cations [65].

Complex **35** represents an even simpler hierarchically composed helical coordination compound. Two mononuclear trisquinolinate zinc complex moieties are connected by a central zinc(II) ion, which binds to the facial orientated oxygen atoms of the quinolinates [66].

4. Summary

This article reviews the metallosupramolecular chemistry of the 8-hydroxyquinoline unit covering the fields of *molecular recognition*, *self-assembly*, and *supramolecular function*:

- *Molecular recognition*: 8-hydroxyquinoline derivatives were described, which are highly selective for specific metal ions and therefore can be used as sensor devices.



34a-H: R = Me
34b-H: R = Et

35 (R = NHCHPhMe, C_7H_{15})

Fig. 14. Hierarchical formation of dinuclear helicate-type complexes.

- *Self-assembly*: supramolecular structures can be assembled from 8-hydroxyquinoline derivatives. This is demonstrated for molecular grids and helicates. Hereby the assembly of heteronuclear metal complexes seems to be especially attractive in this field.
- *Supramolecular function*: due to the electronic structure the quinoline heterocycle shows extraordinary photophysical properties. This can be used to develop materials for devices which are emitting in the visible or in the near IR region.

Just recently 8-hydroxyquinoline was elaborated as a new building block for different purposes in addition to its "classical" use in analytical chemistry. Therefore it seems to be valuable for the design of new materials with predictable properties for novel applications [67].

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