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Hierarchical, Lithium-Templated Assembly of Helicate-Type Complexes: How Versatile Is This Reaction?

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Catechol ligands that bear carbonyl functions such as esters or aldehydes in the 3-position (**1a**–**c**-H_2) form triple-stranded, helicate-type complexes $[Li_3(\mathbf{1a}\text{–}\mathbf{c})_6Ti_2]^-$ with titanium(IV) and the corresponding double-stranded compounds $[Li_2(\mathbf{1a}\text{–}\mathbf{c})_4B_2]$ with boron(III) in hierarchical, lithium-templated processes. The related 8-hydroxyquinoline ligands **2a**,**b**-H can be used for the formation of similar complexes $[Li_3(\mathbf{2a},\mathbf{b})_6M_2]^+$ with cobalt(II), nickel(II), or zinc(II). A prerequisite for the formation of the lithium-bridged dimers is a negative charge of the mononuclear complexes, which are able to electrostatically attract the lithium cations and thus compensate the repulsion between the cations.
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Introduction

Hierarchical processes are frequently observed in the formation of natural and non-natural aggregates.[1–7] The build-up of viruses or proteins, for example, depends on the specific interplay of binding interactions of different strength.[8]

Recently, we described the hierarchical assembly of dinuclear, helicate-type coordination compounds[9–15] that possess three lithium cations bridging mononuclear building blocks. Here, in a first "recognition event", mononuclear catechol complexes are formed that bear carbonyl units in the 3-position of the ligands. These provide a second binding site (Figure 1) that is ideal for the coordination of lithium cations that form three bridging units between two mononuclear moieties in a second "recognition event".[16–26]

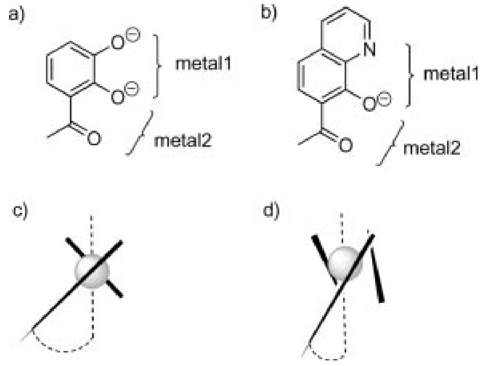

Figure 1. Representation of the two metal binding sites in carbonyl-substituted catecholate (a) and related 8-quinolinate ligands (b) and schematic representations of the relative orientation of chelating ligands in tetrahedral bis-ligand (c) or octahedral tris-ligand complexes (d).

Coordination compounds of this type have been found for derivatives of 3-carbonyl-substituted catechols (carbonyl = aldehyde, ketone, ester) with titanium(IV) and gallium(III) ions. The resulting dinuclear, helicate-type dimers $[Li_3\{(\text{ligand})_6M_2\}]^{n-}$ (M = Ti, $n = 1$; M = Ga, $n = 3$), are in equilibrium with the monomeric complex units. This equilibrium has been thoroughly investigated by NMR spectroscopic and ESI FT-ICR MS methods.[16]

In addition, a related equilibrium was found for monomeric and dimeric catecholate complexes with molybdenum(VI) centers. Here, only two catechols bind to each of the metal centers as the remaining coordination site is blocked by two *cis* arranged oxo units. In case of the dimer, the dioxomolybdenum units take part in the bridging of the three lithium cations.[27]

At first sight the hierarchical assembly of helicates seems to be limited to very special examples. However, in this manuscript we report some new compounds to show that the formation of such helicate-type complexes is more general and is not limited to triple-stranded systems or catechol ligands. We also show that the dimerization depends strongly on the electrostatic attraction between negatively charged metal complexes and lithium cations.

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Results and Discussion

General Considerations

In our recent studies on the hierarchical, lithium-templated assembly of dinuclear, helicate-type complexes, 3-carbonyl-substituted catechol derivatives were used as ligands (see Figure 1, a).[16,27] Compounds of this type provide two binding sites for metal ions: a first metal can be bound to the catecholate unit, while a second metal ion might coordinate to the chelating unit formed by the internal catecholate oxygen atom and the carbonyl oxygen. A tilt angle of 90° between the two chelating units seems to be appropriate in order to allow the formation of the dimeric, lithium-bridged compounds.

A similar geometry to that of the catechol derivatives can be found for 7-carbonyl-substituted 8-hydroxyquinolines (Figure 1, b). Although this ligand has different electronic features compared to the catecholates, it should be able to coordinate two different metal ions and form hierarchically assembled heteronuclear coordination compounds.

Another problem that will be addressed in this study is the formation of double-stranded vs. triple-stranded lithium-bridged dinuclear complexes. Double-stranded coordination compounds are formed if metal cations are introduced that prefer a tetrahedral coordination geometry, while the corresponding triple-stranded systems are formed with octahedral metal centers. Due to the different tilt angles of the projection of the ligand planes on the main axis of the complex unit (see Figure 1c,d), one kind of ligand can form both double- and triple-stranded compounds if the spacer with the lithium cations possesses some flexibility.

In earlier studies we have shown that, due to the donor strength of the carbonyl unit, ester-substituted ligands are the most appropriate to obtain a monomer–dimer equilibrium of lithium-bridged complexes, with the dimer being the dominant species.[16] Therefore we now mainly discuss complexes with the ester-substituted ligands **1a**,**b**-H_2 and **2a**,**b**-H. In addition, we have used 2,3-dihydroxybenzaldehyde (**1c**-H_2) for comparison studies (Figure 2).

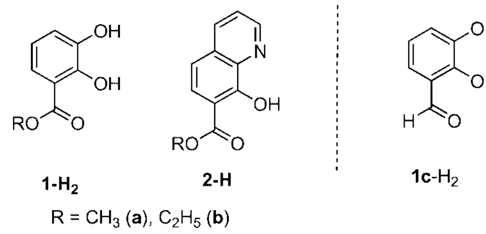
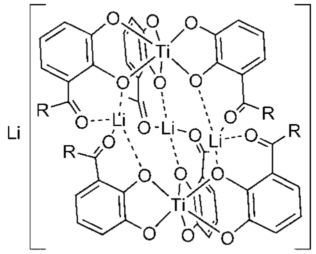


Figure 2. Ester-substituted catechol (**1a**,**b**-H_2) and 8-hydroxyquinoline ligands (**2a**,**b**-H) and 2,3-dihydroxybenzaldehyde (**1c**-H_2).

Triple- and Double-Stranded, Helicate-Type Complexes Based on Catecholate Ligands

Recently we described a series of X-ray structures of dinuclear titanium(IV) complexes of carbonyl-substituted catecholate ligands with aldehyde, ketone, or ester side-chains.[16,28,29]

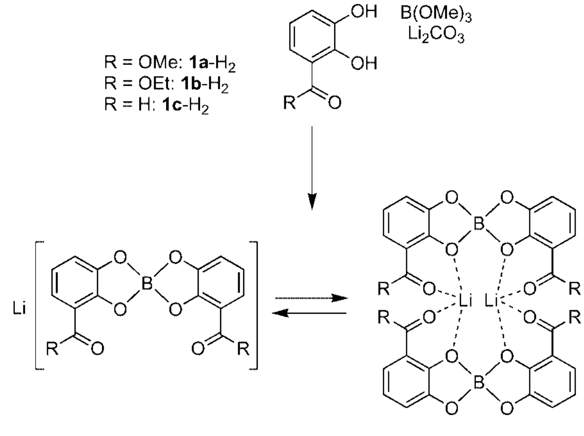
A representation of the dimers Li[Li_3{(**1a**–**c**)$_3$Ti}$_2$] is shown in Figure 3. The side view of the complex shows the two pseudo-octahedral titanium(IV) centers and the bridging tetrahedral lithium cations binding to the carbonyl and to the internal catecholate oxygens.



Li[Li_3(**1a-c**)$_3$$Ti_2$]

Figure 3. Schematic representation of the dimers Li[Li_3{(**1a**–**c**)$_3$Ti}$_2$].

In order to obtain a double-stranded system, we substituted the titanium(IV) ions by boron(III). This ion can only bind two catecholates to form a pseudo-tetrahedral coordination compound. Two of the carbonyl-substituted mononuclear units [(ligand)$_2$B]$^-$ should be able to form a double lithium-bridged dinuclear complex. We performed the reaction of the catechol ligands **1a**–**c** with boric acid in the presence of lithium carbonate.[30] The complexes are still contaminated with free ligand in most cases, and pure material can only be obtained in minor amounts by crystallization (Scheme 1).



Scheme 1.

Well resolved NMR spectra of "Li[(**1a**–**c**)$_2$B]" can be obtained in deuterated chloroform. For example, only one set of signals can be observed for the complex of the aldehyde derivative **1c** in this solvent at δ = 9.08 (s, 1 H), 7.01 (dd, J = 7.7, 1.1 Hz, 1 H), 6.82 (t, J = 7.7 Hz, 1 H) and 6.67 ppm (dd, J = 7.7, 1.1 Hz, 1 H). The high-field shift of the signal of the aldehyde proton to δ = 9.08 ppm seems to be indicative of a dimeric structure for this complex.[16] In this case the aldehyde proton of one complex unit is located in the anisotropic region of the aromatic moieties of the second.

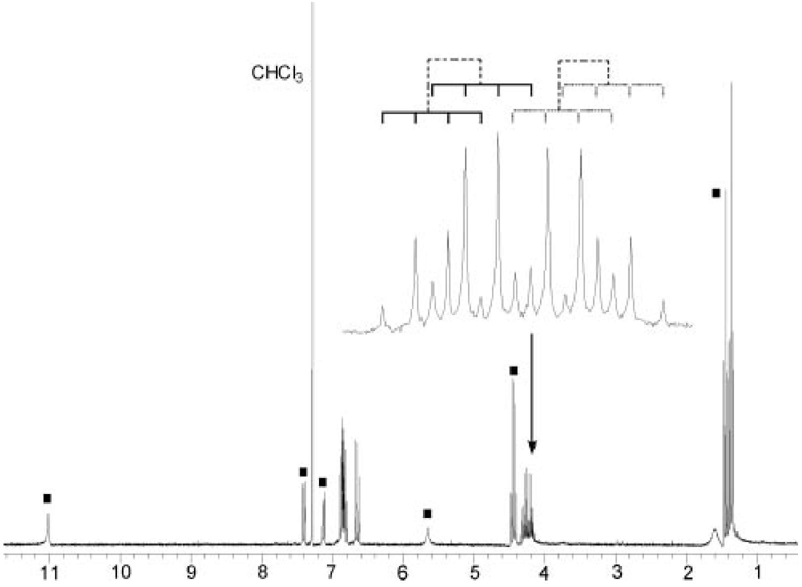


Figure 4. ^{1}H NMR spectrum of "Li[(**1b**)$_2$B]" in deuterated chloroform showing the signals of the complex and the free ligand **1b**-H$_2$ (■). The inset shows the doublet of quartets of the diastereotopic methylene protons in the complex.

Figure 4 shows the ^{1}H NMR spectrum of "Li[(**1b**)$_2$B]" in deuterated chloroform as a representative example. Signals of the free ligand can be observed together with the resonances of the complex. The aromatic protons are observed in the region δ = 6.6–6.9 ppm as multiplets. The most informative resonances can be observed for the ethyl group. The methyl signal is detected as a triplet (J = 7.2 Hz) at δ = 1.37 ppm, while the methylene protons are diastereotopic and appear as two doublets of quartets at δ = 4.19 and 4.28 ppm (J_{gem} = 10.8 Hz). The high-field shifts of the protons of the ethyl ester indicate that a dimeric complex should be present, although no final decision can be made based on the NMR spectra.

The dimeric species [Li$_2${(**1a–c**)$_2$B}$_2$] possess no charge and therefore cannot be detected directly by mass spectrometry. However, we were able to detect characteristic fragments by ESI MS. Peaks of the complexes with ligand **1a** are observed in the negative detection mode at *m*/*z* 343 [(**1a**)$_2$B]$^-$ and 693 [Li{(**1a**)$_2$B}$_2$]$^-$; [K{(**1a**)$_2$B}$_2$]$^-$ is found at *m*/*z* 725 as an impurity. The positive ESI mass spectrum shows a peak for [Li$_3${(**1b**)$_2$B}$_2$]$^+$ at *m*/*z* 763. Fortunately, we were able to obtain X-ray quality crystals of dimeric [Li$_2${(**1a**)$_2$B}$_2$] from chloroform.

The dimer crystallizes in the space group *Cc*, with a noncrystallographic twofold axis perpendicular to the plane formed by the four centers (Li and B). This results in two nonequivalent catecholate ligands, which is in contrast to the high-symmetry spectrum that is observed by NMR spectroscopy. Two of the ligands in the crystal are orientated more or less parallel to the B–B axis, while the others are severely tilted with respect to this axis (Figure 5). This unsymmetrical orientation of the ligands is probably due to the tendency to reduce strain at the bridging lithium cations. The boron and lithium cations adopt a distorted tetrahedral coordination geometry, with B–B, Li–Li, and Li–B separations of 4.456, 4.255, and 3.158–3.187 Å, respectively.

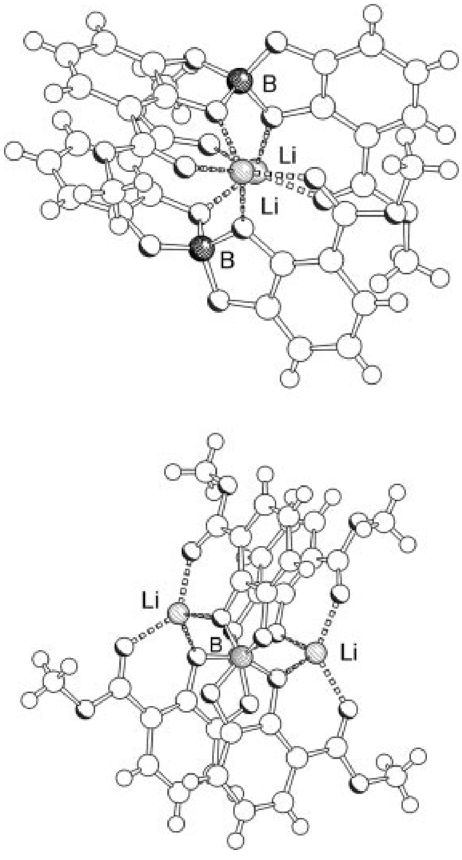


Figure 5. Views of the solid-state structure of dimeric [Li$_2${(**1a**)$_2$B}$_2$] down the Li–Li (top) and down the B–B axis (bottom).

The catecholate complexes with boron show a green or blue fluorescence in chloroform solution. Thus, upon excitation at λ = 265 or 363 nm the aldehyde Li[(**1c**)$_2$B] shows an emission maximum at λ = 476 nm. The corresponding methyl ester shows emission at λ = 393 nm when excited either at λ = 248 or 326 nm.

Triple-Stranded Complexes Based on 8-Hydroxyquinolinate Ligands

8-Hydroxyquinoline and catechol are sterically similar chelating units for metal ions[31] as a five-membered heterocycle is formed upon coordination of the metal. However, their electronic features are severely different. In the deprotonated form, catecholate possesses a charge of 2– while 8-hydroxyquinolinate is a mono anion (see Figure 1). In order to test the versatility of the lithium-templated dimerization of complex units, we decided to substitute the catecholate moiety by 8-hydroxyquinolinate.

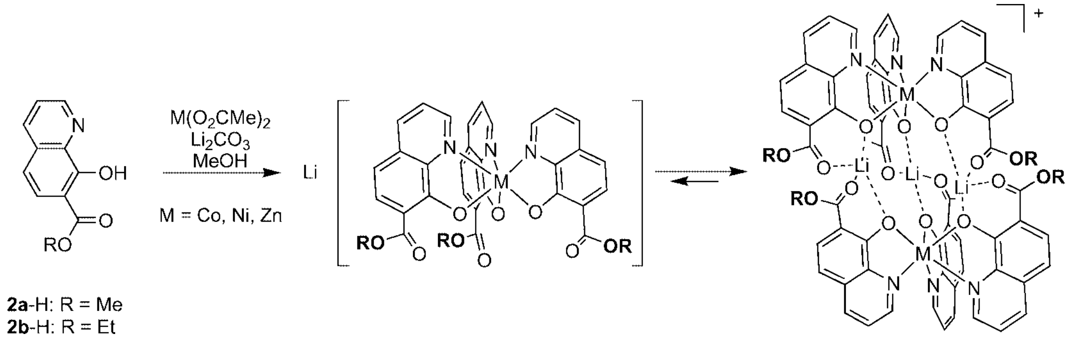
The methyl and ethyl esters **2a**-H and **2b**-H were prepared by simple sulfuric acid catalyzed esterification of 8-hydroxyquinoline-7-carboxylic acid in the corresponding alcohol as solvent.[32]

In initial experiments, coordination studies of ligands **2a/b**-H were performed with aluminium(III) and gallium(III) salts. Elemental analysis of the resulting complexes showed a 3:1 ligand-to-metal ratio. NMR spectroscopy revealed complicated spectra with broad signals, probably due to a *syn/anti* isomerization. However, the positive-ion ESI mass spectra showed the formation of the complexes [(**2a**,**b**)$_3$Ga/Al]. Cationic species can be observed at *m/z* 656 [(**2a**)$_3$AlNa]$^+$, 676 [(**2b**)$_3$AlH]$^+$, 676 [(**2a**)$_3$GaH]$^+$, and 718 [(**2b**)$_3$GaH]$^+$.[33]

Addition of lithium perchlorate to solutions of [(**2a**,**b**)$_3$Ga/Al] in [D$_4$]MeOH does not alter the NMR spectra, and the ESI mass spectra do not show the formation of "{Li$_3$[(**2a**,**b**)$_3$Ga/Al]$_2$}$^{3+}$" dimers. The neutral complex units are obviously not good binders for the lithium cations due to a lack of the electrostatic attraction that it is present in the corresponding compounds of titanium(IV) or gallium(III) with catecholate ligands.

In order to introduce negative charge at the complexes, we switched to cobalt(II), nickel(II), and zinc(II) ions as metal centers (Scheme 2).

The reaction of cobalt(II), nickel(II), or zinc(II) acetate with ligands **2a**,**b**-H in methanol in the presence of lithium carbonate leads, after work-up, to coordination compounds



Scheme 2.

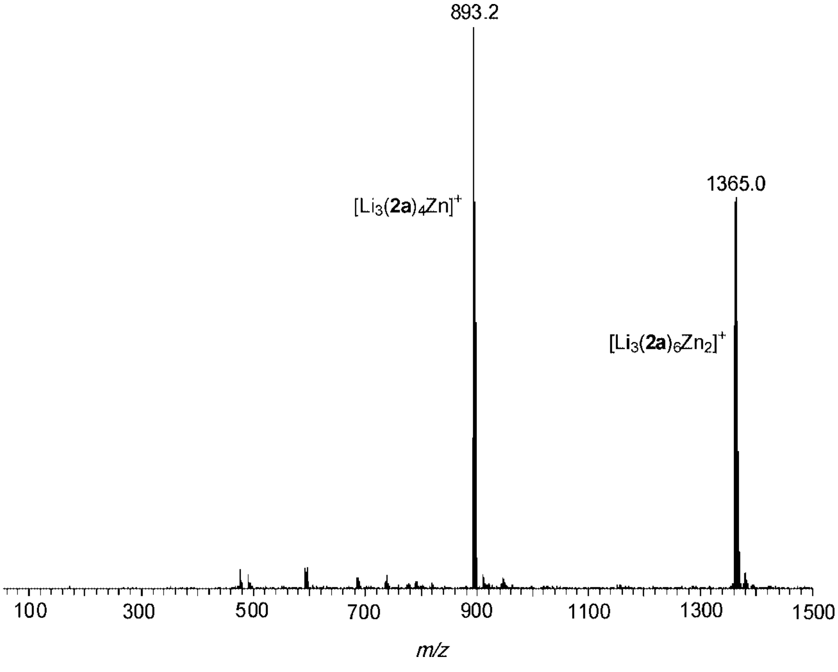


Figure 6. ESI mass spectrum of [Li$_3$(**2**)$_6$Zn$_2$][OAc] in methanol/chloroform.

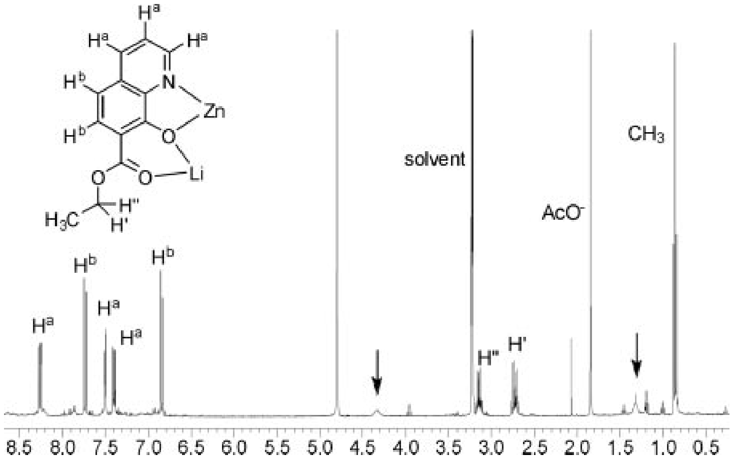


Figure 7. ^{1}H NMR spectrum of $[Li_3(\mathbf{3b})_6Zn_2][O_2CCH_3]$ in [D$_4$]MeOH. The signals of the dimeric complex are assigned. The broad signalsarked with arrows are probably due to monomeric complexes.

that show peaks for the dimeric species $[Li_3(\mathbf{2})_6M_2]^+$ (M = Co, Ni, Zn) at *m*/*z* 1365 $[Li_3(\mathbf{2a})_6Zn_2]^+$, 1449 $[Li_3(\mathbf{2b})_6Zn_2]^+$, 1349 $[Li_3(\mathbf{2a})_6Ni_2]^+$, 1433 $[Li_3(\mathbf{2b})_6Ni_2]^+$, and 1351 $[Li_3(\mathbf{2a})_6Co_2]^+$ in the positive-ion ESI mass spectra. All signals possess the expected isotopic patterns. The spectrum of the zinc(II) complex with ligand **2a** is shown in Figure 6.

A monomeric complex with three ligands is observed only for $[Li_2(\mathbf{2b})_3Ni]^+$ (*m*/*z* 720). The dominating fragmentation is the formation of different mononuclear species. Mononuclear transition metal complexes with four ligands and three lithium cations can be detected in the gas phase at *m*/*z* 893 $[Li_3(\mathbf{2a})_4Zn]^+$, 949 $[Li_3(\mathbf{2b})_4Zn]^+$, 887 $[Li_3(\mathbf{2a})_4Ni]^+$, 943 $[Li_3(\mathbf{2b})_4Ni]^+$, and 889 $[Li_3(\mathbf{2a})_4Co]^+$. This shows an unsymmetrical decomposition of the dimer under these ionization conditions with loss of the neutral mononuclear $[(\mathbf{2a},\mathbf{b})_2Zn/Ni/Co]$.[16]

The diamagnetic zinc(II) complexes can be studied by NMR spectroscopy. The spectrum of "$Li[(\mathbf{2b})_3Zn]$" in [D$_4$]-MeOH is shown in Figure 7 as a representative example.

The dinuclear zinc(II) complex $[Li_3(\mathbf{3b})_6Zn_2][O_2CCH_3]$ is observed as the dominant species. The signals of the three pyridine protons H^a appear at δ = 8.26 (dd, *J* = 8.2, 1.7 Hz), 7.50 (dd, *J* = 4.2, 1.7 Hz), and 7.39 ppm (dd, *J* = 8.2, 4.2 Hz) while the doublets (*J* = 9.5 Hz) of the phenolic unit H^b are detected at δ = 7.73 and 6.82 ppm. The terminal CH$_3$ group of the ethyl ester is found as a triplet (*J* = 7.1 Hz) at δ = 0.86 ppm. The methylene group results in two doublets of quartets at δ = 2.72 and 3.14 ppm, with a geminal coupling constant 11.0 Hz. The high-field shift and the diastereotopicity of those two signals show that the dimeric complex is present, as (1) in the dimeric complex the ethyl groups of one complex unit are located close to the aromatic system of the second. This leads to an anisotropic shift to low field. This effect is also observed for the resonance of the methyl group. (2) In the dimeric complex the stereochemistry at the complex units is fixed so no fast racemization between the Λ and Δ isomers takes place. In the monomers this isomerization as well as a *syn–anti* isomerization should proceed much more rapidly. According to this, broad signals at δ = 4.33 and 1.31 ppm (marked by an arrow in Figure 7) can be tentatively assigned to the ethyl groups of a highly dynamic mononuclear complex.

We were able to obtain X-ray quality crystals of $[Li_3(\mathbf{2b})_6Ni_2][HSO_4]\cdot Et_2O$ from ethanol/diethyl ether. The structure of the $[Li_3(\mathbf{2b})_6Ni_2]^+$ cation is depicted in Figure 8.[34] This compound is built up from two pseudo-octahedral nickel(II) complexes $[(\mathbf{2b})_3Ni]^-$ with the quinolinate ligands **2b** orientated in a *syn* fashion. This enables the binding of three lithium cations to the phenolate carbonyl

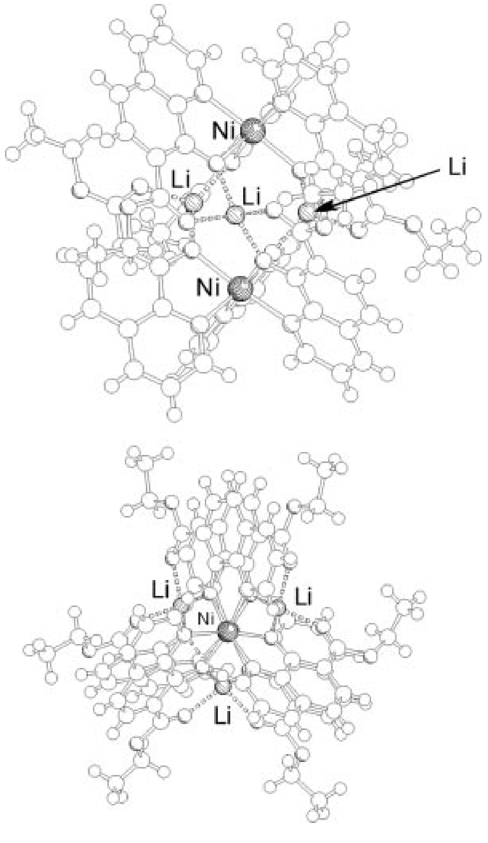


Figure 8. Views of the solid-state structure of the cation $[Li_3\{(\mathbf{2b})_3Ni\}_2]$ down the Li–Li (top) and down the Ni–Ni axis (bottom).

chelate of each of the two units and formation of the triply bridged dimer, with nickel–nickel separations of 5.276 Å. The three lithium cations form a triangle with distances of 3.607, 3.804, and 3.825 Å, respectively. The alkali metal ions are located 3.374–3.462 Å away from the transition metals.

The structure of the hydroxyquinoline complex $[Li_3(\mathbf{2b})_6Ni_2]^+$ is very similar to those observed for titanium(IV) catechol derivatives like $[Li_3\{(\mathbf{1b})_3Ti\}_2]^-$.

Conclusions

We have studied the versatility of the lithium-templated hierarchical assembly of dinuclear, helicate-type complexes. As described earlier, titanium(IV) catecholate complexes that bear carbonyl substituents in the 3-position of the ligand are able to form triple-stranded dimers in the presence of lithium cations.[16] Substitution of the titanium(IV) centers by boron results in the formation of the analogous double-stranded complexes, which, although they are labile and are often obtained in a mixture with free ligand, can be readily characterized.

Furthermore, this approach to oligonuclear complexes is not restricted to catecholate ligands as 8-hydroxyquinolines with a carbonyl in the 7-position can form related compounds with late transition metals. With aluminum(III) or gallium(III) ions neutral 8-hydroxyquinolinate complexes are obtained, which do not show a tendency to lithium-mediated dimerization. This indicates that the electrostatic attraction between anionic complex units and lithium cations is an essential driving force in the dimerization process.

We have a broad set of different kinds of ligands and different metal centers available for future studies. We will investigate whether we can use "combinatorial" approaches to obtain specific heterodinuclear complexes and we will functionalize the periphery of the complexes in order to tune their properties.

Experimental Section

NMR spectra were recorded with a Varian Mercury 300 or Inova 400 spectrometer. FT-IR spectra were recorded with a Bruker IFS spectrometer. Mass spectra were recorded with a Thermo Deca XP mass spectrometer. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyser. Fluorescence measurements were performed on a Perkin–Elmer LS-50B spectrofluorimeter.

$Li[Li_3(1a–c)_6Ti_2]$: The titanium(IV) complexes were prepared as described earlier.[16]

General Procedure for the Preparation of Boron Complexes: Catechol **1a**–**c**-H_2 (2 equiv.), boric acid (1 equiv.), and lithium carbonate (1 equiv.) were dissolved in methanol (10 mL) and the solution stirred overnight. The solvent was then removed and the residue was recrystallized from chloroform and dried in vacuo. Attempts to purify the compounds over Sephadex LH20 did not result in pure material.

$Li_2[B_2(1a)_4]$: Yield: 40 mg (42%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.77 (m, 8 H), 6.57 (t, J = 8.0 Hz, 4 H), 3.71 ppm (s, 12 H). IR (KBr): $\tilde{\nu}$ = 3460, 2361, 2340, 1678, 1469, 1322, 1262, 1227, 1143, 1107, 1031, 744 cm^{-1}. Negative ESI MS (dmf, MeOH): m/z 693 $[LiB_2(\mathbf{1a})_4]^-$, 343 $[B(\mathbf{1a})_2]^-$. Fluorescence data: ($CHCl_3$): λ_{ex} (nm) = 248, 326; λ_{em} (nm) = 395. $C_{32}H_{24}B_2Li_2O_{16}\cdot 4H_2O$ (772.10): calcd. C 49.77, H 4.18; found C 49.98, H 4.69. A single crystal of the product was selected and mounted on a cryo-loop for single-crystal X-ray data collection on a Bruker–Nonius KAPPACCD diffractometer equipped with a graphite-monochromated Mo-K_α radiation source (λ = 0.71073 Å), an APEXII area detector, and an Oxford Cryostream cryogenic device (data collected at 173 K). Structure solution was performed with SHELXS-97,[35] with subsequent refinement on F^2 by full-matrix least-squares (SHELXL-97[35]). Hydrogen atoms were calculated at their idealized positions and refined with a riding model (isotropic displacement parameters 1.2- or 1.5-times C anisotropic displacement parameters). Multiscan absorption correction was applied to the data (SADABS[12]). Crystal system: monoclinic; space group: *Cc*; a = 9.2853(19), b = 23.783(5), c = 14.844(3) Å, β = 106.70(3)°; cell volume: 3139.7(11) $Å^3$; Z = 4; calculated density: 1.481 $g\,cm^{-3}$; absorption coefficient: 0.117 mm^{-1}; $F(000)$ = 1440; crystal color: colorless; size: $0.40 \times 0.20 \times 0.10$ mm^3; reflections for cell refinement: 1005 (θ range 2.5 to 27.5°); data collection method: &phis; and ω scans; θ range for data collection: 3.4 to 27.4°; index ranges: $-11 \le h \le 11$, $0 \le k \le 30$, $0 \le l \le 19$; completeness to θ = 27.4°: 97.2%; reflections collected: 3470; independent reflections: 3470 (R_{int} = 0.0654, before merging); reflections with $F^2 > 2\sigma$: 2416; absorption correction: semi-empirical from equivalents; Min. and max. transmission: 0.9546 and 0.9884; structure solution: direct methods; full-matrix least-squares on F^2; weighting parameters: a = 0.0449, b = 0.1095; data/restraints/parameters: 3470/2/470; final R indices [$F^2 > 2\sigma$] R_1 = 0.0632, wR_2 = 0.1064; R indices (all data) R_1 = 0.1141, wR_2 = 0.1293; goodness-of-fit on F^2: 1.190; absolute structure parameter: 1.0(14); extinction coefficient: 0.0020(4); largest and mean shift/su: 0.001 and 0.000; largest diff. peak and hole: 0.23 and –0.28 $e\,Å^{-3}$.

$Li_2[B_2(1b)_4]$: Yield: 39 mg (38%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.85 (m, 8 H), 6.64 (t, J = 7.2 Hz, 4 H), 4.19 (qd, J = 7.2, 10.8 Hz, 4 H), 4.28 (qd, J = 7.2, 10.8 Hz, 4 H), 1.36 ppm (t, J = 7.2 Hz, 12 H). IR (KBr): $\tilde{\nu}$ = 3474, 2983, 2361, 2369, 1675, 1468, 1372, 1263, 1222, 1102, 1033, 885, 742 cm^{-1}. Positive ESI MS ($CHCl_3$, MeOH): m/z 763 $[Li_3B_2(\mathbf{1b})_4]^+$, 385 $[Li_2B(\mathbf{1b})_2]^+$. Fluorescence data: ($CHCl_3$): λ_{ex} (nm) = 255, 328; λ_{em} (nm) = 395. $C_{36}H_{32}B_2Li_2O_{16}\cdot 7H_2O$ (882.25): calcd. C 49.01, H 5.25; found C 48.86, H 5.46.

$Li_2[B_2(1c)_4]$: Yield: 57 mg (54%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 9.08 (s, 1 H), 7.00 (dd, J = 7.6, 1.1 Hz, 1 H), 6.83 (t, J = 7.6 Hz, 1 H), 6.67 ppm (dd, J = 7.6, 1.1 Hz, 1 H). IR (KBr): $\tilde{\nu}$ = 3854, 3744, 3420, 2361, 2340, 1661, 1621, 1585, 1467, 1403, 1266, 1214, 1086, 880, 737, 680 cm^{-1}. Negative ESI MS (dmf, MeOH): m/z 573 $[LiB_2(\mathbf{1c})_4]^-$, 283 $[B(\mathbf{1c})_2]^-$. Fluorescence data: ($CHCl_3$): λ_{ex} (nm) = 265, 363; λ_{em} (nm) = 471. $C_{28}H_{16}B_2Li_2O_{12}$ (579.93): calcd. C 57.99, H 2.78; found C 58.21, H 3.26.

General Procedure for the Preparation of Aluminum(III) and Gallium(III) Complexes of the 8-Hydroxyquinoline Ligands 2a,b-H: 8-Hydroxyquinoline derivative **2a**-H or **2b**-H (3 equiv.) and gallium nitrate or aluminum trichloride (1 equiv.) were dissolved in methanol or ethanol and stirred overnight. The solvent was then removed under reduced pressure to obtain solid materials in close to quantitative yields.

$[(2a)_3Al]$: Yield: 59.1 mg (92%). ^1H NMR (400 MHz, CD_3OD): δ = 3.96 (s, 3 H), 7.34 (d, J = 8.8 Hz, 1 H), 7.60 (dd, J = 4.2, 8.3 Hz, 1 H), 7.86 (d, J = 8.8 Hz, 1 H), 8.26 (dd, J = 1.1, 8.3 Hz, 1 H), 8.80 ppm (dd, J = 1.1, 4.2 Hz, 1 H). Positive ESI MS: m/z 656

[Na(**2a**)$_3$Al] $^+$. IR (KBr): $\tilde{\nu}$ = 3431, 3056, 2990, 2948, 2843, 1702, 1629, 1605, 1572, 1501, 1459, 1397, 1317, 1291, 1247, 1195, 1123, 1055, 1009, 984, 916, 882, 789, 757, 667, 621, 575, 474, 458 cm^{-1}. $C_{33}H_{24}AlN_3O_9{\cdot}1.5\,H_2O{\cdot}1.5\,CH_3OH$ (708.64): calcd. C 58.48, H 4.69, N 5.93; found C 58.56, H 4.73, N 5.93.

[(2b)$_3$Al]: Yield: 52.2 mg (98%). ^{1}H NMR (400 MHz, CD_3OD): Due to the presence of different isomers only an uninformative spectrum with broad signals is obtained. Positive ESI MS: *m/z* 676 [H(**2b**)$_3$Al]$^+$. IR (KBr): $\tilde{\nu}$ = 3791, 3447, 3066, 2980, 2931, 2901, 1707, 1603, 1572, 1501, 1458, 1399, 1311, 1292, 1244, 1197, 1112, 1055, 1024, 948, 884, 833, 755, 666, 622, 573, 529, 492 cm^{-1}. $C_{36}H_{30}AlN_3O_9{\cdot}H_2O$ (693.65): calcd. C 62.34, H 4.65, N 6.06; found C 62.35, H 4.98, N 5.97.

[(2a)$_3$Ga]: Yield: 56.7 mg (97%). ^{1}H NMR (400 MHz, CD_3OD): δ = 3.59 (s, 3 H), 7.23 (d, J = 8.8 Hz, 1 H), 7.45 (d, J = 8.8 Hz, 1 H), 7.61 (d, J = 8.2 Hz, 1 H), 7.63 (d, J = 8.2 Hz, 1 H), 7.95 ppm (d, J = 8.8 Hz, 1 H). Positive ESI MS: *m/z* 676 [H(**2a**)$_3$Ga]H$^+$. IR (KBr): $\tilde{\nu}$ = 3898, 3854, 3744, 3694, 3674, 3620, 3589, 3565, 3437, 2948, 2360, 2339, 1842, 1700, 1652, 1564, 1504, 1456, 1391, 1317, 1293, 1243, 1197, 1117, 1058, 1005, 884, 834, 748, 666, 610, 561, 509 cm^{-1}. $C_{33}H_{24}GaN_3O_9{\cdot}2\,H_2O$ (712.32): calcd. C 55.64, H 3.96, N 5.90; found C 55.69, H 3.99, N 6.01.

[(2b)$_3$Ga]: Yield: 49.1 mg (89%). ^{1}H NMR (400 MHz, CD_3OD): Due to the presence of different isomers only an uninformative spectrum with broad signals was obtained. Positive ESI MS: *m/z* 718 [H(**2b**)$_3$Ga]$^+$. IR (KBr): $\tilde{\nu}$ = 3511, 3408, 3063, 2979, 2934, 2901, 1711, 1603, 1569, 1500, 1452, 1395, 1311, 1291, 1243, 1196, 1119, 1054, 1022, 948, 833, 788, 747, 665, 607, 563, 521 cm^{-1}. No correct elemental analysis was obtained.

General Procedure for the Preparation of Cobalt(II), Nickel(II), and Zinc(II) Complexes of the 8-Hydroxyquinoline Ligands 2a,b-H: 8-Hydroxyquinoline derivative **2a**-H or **2b**-H (3 equiv.), lithium carbonate, and cobalt(II), nickel(II) or zinc(II) acetate (1 equiv.) were dissolved in methanol or ethanol and stirred overnight. The solvent was removed under reduced pressure to obtain solid materials in close to quantitative yields.

[Li$_3$(2a)$_6$Co$_2$][O$_2$CCH$_3$]: Yield: 24 mg (97%) as crude product. IR (KBr): $\tilde{\nu}$ = 3448, 2952, 1680, 1600, 1562, 1500, 1449, 1404, 1384, 1307, 1245, 1198, 1117, 1008, 833, 797, 752, 671, 616, 536, 462 cm^{-1}. Positive ESI MS: *m/z* 1351 [Li$_3$(**2a**)$_6$Co$_2$]$^+$. No correct elemental analysis was obtained, probably due to the exchange of acetate by other anions.

[Li$_3$(2a)$_6$Ni$_2$][O$_2$CCH$_3$]: Yield: 56.9 mg (98%). Positive ESI MS: *m/z* 1349 [Li$_3$(**2a**)$_6$Ni$_2$]$^+$. IR (KBr): $\tilde{\nu}$ = 3411, 3049, 2999, 2949, 1680, 1601, 1556, 1500, 1447, 1403, 1308, 1246, 1193, 1152, 1116, 1051, 1006, 883, 829, 788, 746, 669, 611, 536, 472 cm^{-1}. $C_{66}H_{48}Li_3N_6Ni_2O_{18}{\cdot}OCOCH_3{\cdot}2\,CH_3OH$ (1474.5): calcd. C 57.02, H 4.03, N 5.70; found C 57.36, H 4.26, N 5.93.

[Li$_3$(2b)$_6$Ni$_2$][HSO$_4$]: The complex was prepared using **2b**-H·H_2SO_4 as ligand. Yield: 55.8 mg (95%). Positive ESI MS: *m/z* 1432.9 [Li$_3$(**2b**)$_6$Ni$_2$]$^+$. IR (KBr): $\tilde{\nu}$ = 3425, 3056, 2979, 2932, 1677, 1599, 1557, 1500, 1450, 1406, 1361, 1305, 1244, 1191, 1157, 1115, 1026, 950, 828, 785, 744, 667, 616, 538, 493, 458 cm^{-1}. $C_{72}H_{60}Li_3N_6Ni_2O_{18}{\cdot}HSO_4{\cdot}C_2H_5OH$ (1578.66): calcd. C 56.30, H 4.28, N 5.32; found C 56.54, H 4.47, N 5.21.

X-ray Crystal Structure Analysis for [Li$_3$(2b)$_6$Ni$_2$][HSO$_4$]: Formula: $[C_{72}H_{60}Li_3N_6Ni_2O_{18}][HSO_4]{\cdot}C_4H_{10}O$; M = 1606.69; yellow crystal, $0.20\times0.15\times0.06$ mm^3; a = 12.763(1), b = 16.435(1), c = 18.420(1) Å, α = 83.93(1)°, β = 78.12(1)°, γ = 87.00(1)°; V = 3758.0(4) Å^3; ρ_{calc} = 1.420 g cm^{-3}; μ = 0.610 mm^{-1}; empirical absorption correction ($0.888 \le \theta \le 0.964$); Z = 2, triclinic, space group $P\bar{1}$ (no. 2); λ = 0.71073 Å; T = 198 K; ω and φ scans, 24802 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.54 Å^{-1}; 9777 independent (R_{int} = 0.078) and 6454 observed reflections [$I \ge 2\sigma(I)$]; 1008 refined parameters, R = 0.078, wR_2 = 0.231, max. residual electron density 2.51 (–0.82) e Å^{-3} in the region of the disordered anion, which was refined with geometrical and thermal constraints; hydrogen atoms were calculated and refined as riding. The data set was collected with a Nonius KappaCCD diffractometer equipped with a rotating anode generator. Programs used: data collection: COLLECT (Nonius B.V., 1998); data reduction: Denzo-SMN;[36] absorption correction: SORTAV;[37,38] structure solution: SHELXS-97;[39] structure refinement: SHELXL-97 (G. M. Sheldrick, University of Göttingen, 1997); graphics: SCHAKAL (E. Keller, University of Freiburg, 1997).

[Li$_3$(2a)$_6$Zn$_2$][O$_2$CCH$_3$]: Yield: 56.1 mg (96%). ^{1}H NMR (400 MHz, CD_3OD): δ = 1.79 (s, 3 H), 2.64 (s, 3 H), 6.86 (d, J = 9.0 Hz, 1 H), 7.40 (dd, J = 3.9, 8.2 Hz, 1 H), 7.50 (dd, J = 1.2, 3.9 Hz, 1 H), 7.69 (d, J = 9.0 Hz, 1 H), 8.26 ppm (dd, J = 1.2, 8.2 Hz, 1 H). positive ESI MS: *m/z* 1365.4 [Li$_3$(**3a**)$_6$Zn$_2$]$^+$. IR (KBr): $\tilde{\nu}$ = 3986, 3946, 3661, 3428, 3053, 2949, 1682, 1601, 1557, 1500, 1449, 1405, 1308, 1248, 1194, 1153, 1116, 1056, 1008, 908, 827, 788, 743, 701, 670, 616, 543, 479 cm^{-1}. $C_{66}H_{48}Li_3N_6O_{18}Zn_2{\cdot}OCOCH_3{\cdot}3\,H_2O{\cdot}3\,CH_3OH$ (1573.9): calcd. C 54.18, H 4.42, N 5.34; found C 54.10, H 4.33, N 5.48.

[Li$_3$(2b)$_6$Zn$_2$][O$_2$CCH$_3$]: Yield: 56.5 mg (98%). ^{1}H NMR (400 MHz, CD_3OD): δ = 0.86 (t, J = 7.1 Hz, 3 H), 1.84 (s, 3 H), 2.72 (dd, J = 3.5, 7.1 Hz, 1 H), 3.14 (dd, J = 3.5, 7.1 Hz, 1 H), 6.84 (d, J = 8.8 Hz, 1 H), 7.40 (dd, J = 4.7, 8.2 Hz, 1 H), 7.50 (dd, J = 1.4, 4.7 Hz, 1 H), 7.73 (d, J = 8.8 Hz, 1 H), 8.26 ppm (d, J = 1.4, 8.2 Hz, 1 H). Positive ESI MS: *m/z* 1449 [Li$_3$(**3b**)$_6$Zn$_2$]$^+$. IR (KBr): $\tilde{\nu}$ = 3415, 3057, 2979, 2932, 2902, 1678, 1601, 1556, 1500, 1450, 1408, 1362, 1304, 1245, 1190, 1156, 1116, 1027, 950, 828, 786, 742, 672, 616, 539, 494, 468 cm^{-1}. $C_{72}H_{60}Li_3N_6O_{18}Zn_2{\cdot}OCOCH_3{\cdot}2\,H_2O{\cdot}CH_3OH$ (1576.0): calcd. C 57.16, H 4.54, N 5.33; found C 57.14, H 4.78, N 5.42.

CCDC-620597 and -620598 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.uk/data_request/cif.

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