This article is published as part of the *Dalton Transactions* themed issue entitled:

Self-Assembly in Inorganic Chemistry

Guest Editors Paul Kruger and Thorri Gunnlaugsson

Published in issue 45, 2011 of *Dalton Transactions*

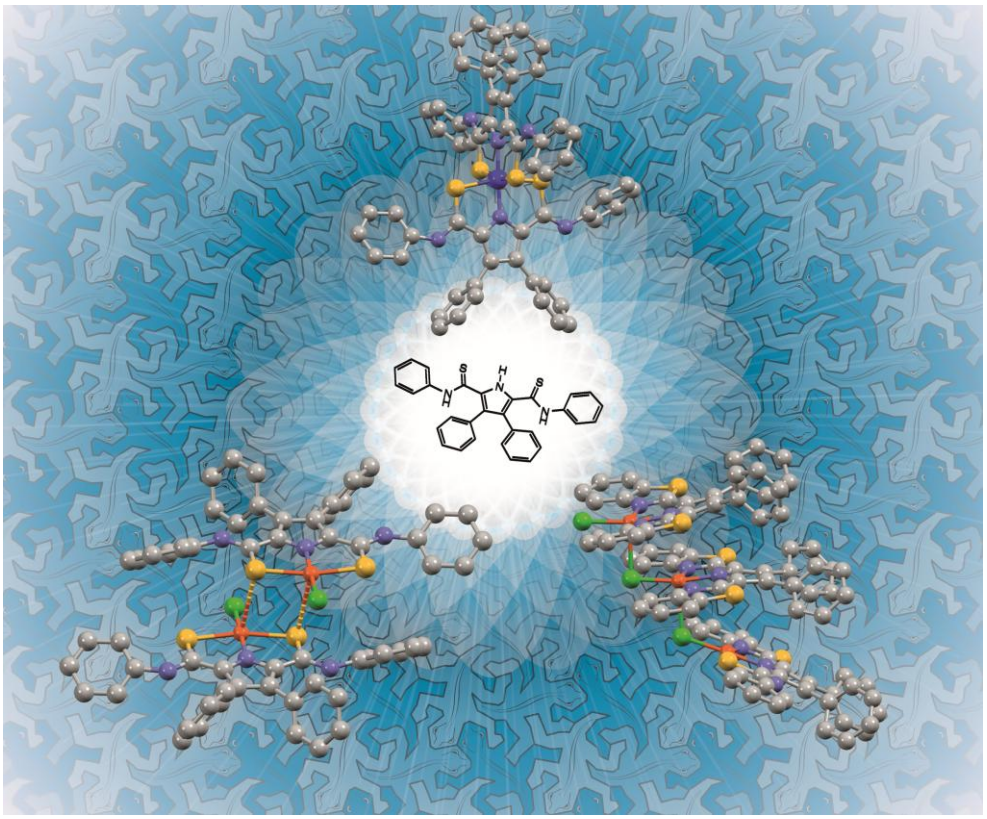


Image reproduced with permission of Mark Ogden

Articles in the issue include:

PERSPECTIVE:

ARTICLES:

Visit the *Dalton Transactions* website for more cutting-edge inorganic and organometallic research
www.rsc.org/dalton

Dalton Transactions

Dynamic Article Links

Cite this: *Dalton Trans.*, 2011, **40**, 12067

www.rsc.org/dalton

PAPER

Decorating the lanthanide terminus of self-assembled heterodinuclear lanthanum(III)/gallium(III) helicates†

Markus Albrecht,*[a] Irene Latorre,[a] Gent Mehmeti,[a] Konstantin Hengst[a,b] and Iris M. Oppel[b]

Received 28th April 2011, Accepted 15th July 2011
DOI: 10.1039/c1dt10775e

Arylacylhydrazones of 2,3-dihydroxybenzaldehyde are appropriate ligands for the preparation of heterodinuclear triple-stranded helicates involving high coordinated lanthanide(III) ions. In the present study, three different kinds of substituents are introduced at the ligands in order to modify the organic periphery of the coordination compounds: (1) alkoxy groups are attached to the terminal phenyl groups, (2) NH protons of the hydrazones are substituted by phenyl moieties and (3) amino acid bearing units are attached to the terminus of the ligand. The new ligands nicely form the desired triple-stranded gallium(III)-lanthanum(III) complexes [(**5a-c,7,12,15**)$_3$GaLa] of which the highly phenylated derivative was crystallized and studied by X-ray diffraction.

Introduction

Metallosupramolecular chemistry is based on the reversible recognition between metal ions and oligotopic ligands.[1] Complicated structures are obtained by simply mixing of organic ligands with appropriate metal ions.[2] If heterotopic ligands are introduced, it is possible to isolate coordination compounds containing different metal ions in well defined positions. Especially the latter are of high importance in order to study metal-metal communication phenomena.[3]

A very simple class of metallosupramolecular compounds are the helicates.[4] They are formed in self-assembly processes starting from linear oligotopic ligand strands and two or more metal ions. The introduction of different metal ions to obtain heterodinuclear complexes is challenging but was described in some cases and utilizes either different electronic features or different denticity of ligand units to distinguish between the different metal ions. The latter allows for example the formation of heterodinuclear p-f or d-f coordination compounds which in some cases exhibit interesting energy transfer between complex units.[5]

Recently we introduced a simple system, in which triple-stranded heterodinuclear complexes are formed from acyl- (**A**)[6] or tosyl-hydrazones (**B**)[7] of 2,3-dihydroxybenzaldehyde. The catechol unit acts as a bidentate ligand and coordinates *e.g.* titanium(IV), aluminum(III) or gallium(III)ions, while the acyl or tosyl hydrazone together with the internal catechol oxygen atoms represents a tridentate ligand for binding of high coordinated metal ions (*e.g.* lanthanides). A remarkable difference between the acyl and the tosyl derivatives is that in **A** the ligands are more or less linear, while in **B** a kink is introduced by the tetrahedral sulphur atom leading to back folding of the substituent and a more compressed overall shape (Fig. 1).

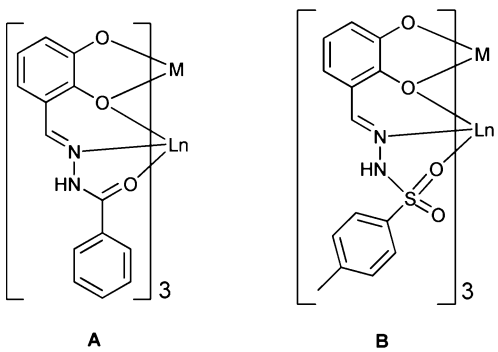


Fig. 1 Heteroditopic helicates based on acyl- (**A**) or tosyl-hydrazones (**B**) of 2,3-dihydroxybenzaldehyde.

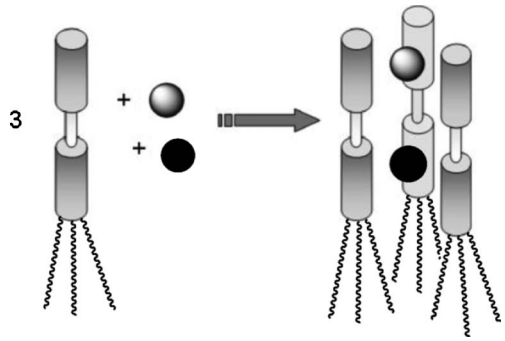
The simple preparation of those ligands for self-assembly of heterodinuclear compounds allows a facile variation of the substituents in the periphery. In here we describe different approaches to functionalized helicates of type **A**. First, terminal aryl substituents are introduced, which bear alkyl chains of different length. This leads to compounds with a hydrophobic lanthanide moiety. Second, the NH proton of the acylhydrazone is substituted by a phenyl group, resulting in an accumulation of six phenyl substituents around the lanthanide complex. Finally, amino acid based residues are attached to the "lanthanide terminus" of the ligand in order to provide derivatives which in the future can be used for the attachment of *e.g.* short peptides.

[a]*Institut für Organische Chemie, Landoltweg 1, 52074, Aachen, Germany. E-mail: markus.albrecht@oc.rwth-aachen.de*
[b]*Institut für Anorganische Chemie, Landoltweg 1, 52074, Aachen, Germany*
† CCDC reference number 789894. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10775e

Results and discussion

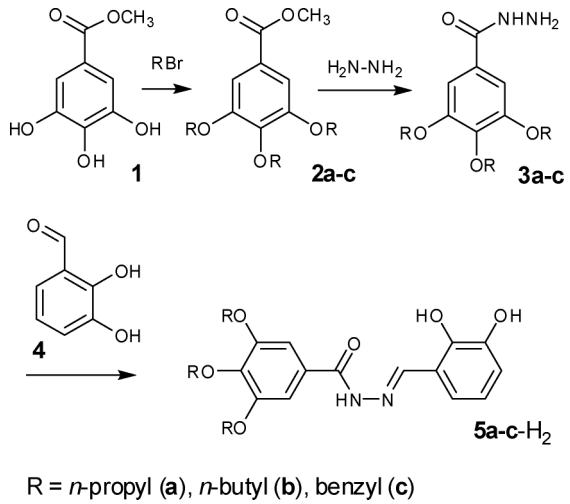
Alkyl-substituted heterodinuclear triple-stranded helicates

In general, alkyl-functionalization at the acylhydrazone terminus of the ligand results in coordination compounds in which all alkyl groups are orientated in the same direction of space. This is schematically presented in Scheme 1.



Scheme 1 Schematic representation of the formation of heterodinuclear helicates which bear an "alkyl-bundle" at the tail.

The preparation of the required ligands **5a-c**-H follows the reaction sequence as outlined in Scheme 2. It starts with methylgallate **1** which easily is prepared from commercially available gallic acid.[8] The alkyl chains are introduced by a Williamson ether synthesis. It is found that in this step the length of the carbon chains influences the conditions required for the reaction.



Scheme 2 Preparation of ligands **5a-c**-H_2.

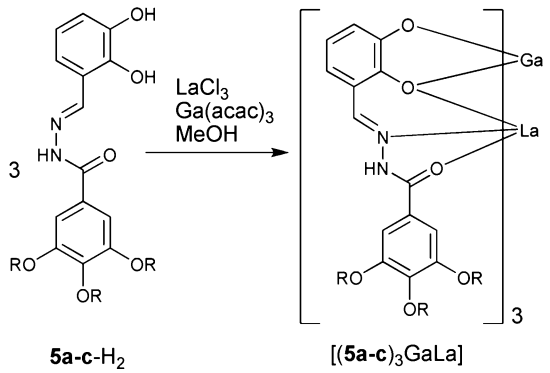
The introduction of the propyl chain, to obtain the intermediate **2a**, proceeds in 84% yield within 6 h. DMF is used as solvent instead of acetone, which was reported in the literature.[9] With acetone too long reaction times are required leading to significant decomposition of the product. In contrast to this, it has been possible to easily introduce the butyl chain (**2b**) in acetone (80%). Both compounds **2a** and **2b** show good solubility in water indicating only weak hydrophobic influence of the alkyl chains.

As aromatic substituent a benzylic group was introduced following as well the Williamson ether synthesis. **2c** was obtained after 24 h by reflux in acetone (92%).

The second step of the sequence to afford the ligands was the preparation of the hydrazides by reaction of the esters with hydrazine monohydrate. Products **3a** and **3b** were obtained from **2a** and **2b** in 70% or quantitative, respectively, after 24 h at room temperature in MeOH. This probably was possible due to the good solubility of the intermediates **2a** and **2b** in polar solvents. Compound **3c** was obtained from **2c** and hydrazine after reflux in MeOH for 48 h in a yield of 51%.

Finally, standard hydrazone condensation of derivatives **3a–3c** with 2,3-dihydroxybenzaldehyde **4** in methanol afforded after 24 h the ligands **5a**-H_2 - **5c**-H_2.[10]

With the obtained ligands, complexes [(**5a**)$_3$GaLa], [(**5b**)$_3$GaLa] and [(**5c**)$_3$GaLa] were successfully synthesized and were characterized by NMR spectroscopy and MS-spectrometry. The coordination studies were performed following Scheme 3.



Scheme 3 Formation of the heterodinuclear La-Ga helicates [(**5a-c**)$_3$GaLa] from the corresponding ligands. [(**5c**)$_3$GaLa] with six terminal benzyl groups can be described as a generation 0 (G0) dendritic unit.[11]

As a representative example the NMR spectra of complex [(**5b**)$_3$GaLa] as well as of the free ligand **5b**-H_2 are depicted in Fig. 2. The protons of the catecholate OH disappear upon coordination. Especially the NH proton is strongly influenced and is shifted from $\delta = 11.12$ to 12.45. The other resonances experience a high field shift. E.g., the aromatic protons are shifted from $\delta =$ 6.75–6.97 to $\delta = 6.32$–6.48.

A hexaphenyl-substituted heterodinuclear triple-stranded helicate

In ligands of type **A**, substituents at the acyl unit can be easily varied in the preparation of the ligand. However, it was also of interest to substitute the NH proton in order to protect this position against deprotonation and to introduce additional branching. Therefore the known phenyl acyl hydrazone **6**[12] was condensed with aldehyde **4** to obtain ligand **7**-H_2. Coordination studies with gallium(III) as well as lanthanum(III) salts resulted in the formation of the heterodinuclear helicate [(**7**)$_3$GaLa] (Scheme 4).

The complex [(**7**)$_3$GaLa] was characterized by spectroscopic methods. The NMR spectrum shows the peak of the imine proton at $\delta = 7.84$ (s, 3H), the aromatic resonances of the phenyl groups at $\delta = 7.45$ (m, 15 H), 6.98 (t, $J = 7.4$ Hz, 3 H), 6.76 (d, $J = 7.4$ Hz, 6 H), 6.50 (d, $J = 7.4$ Hz, 6 H), and the catechol signals at $\delta =$ 6.38 (t, $J = 7.7$ Hz, 3 H), 6.08 (m, 6 H). Positive ESI MS reveals the dominating molecular peak of the protonated species at $m/z =$ 1199.33.

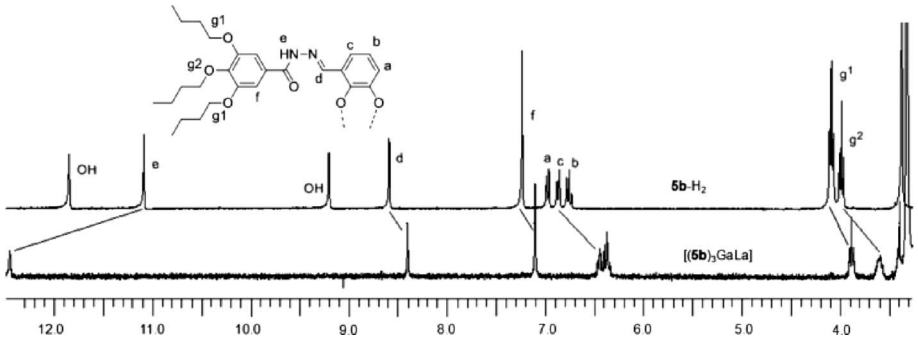
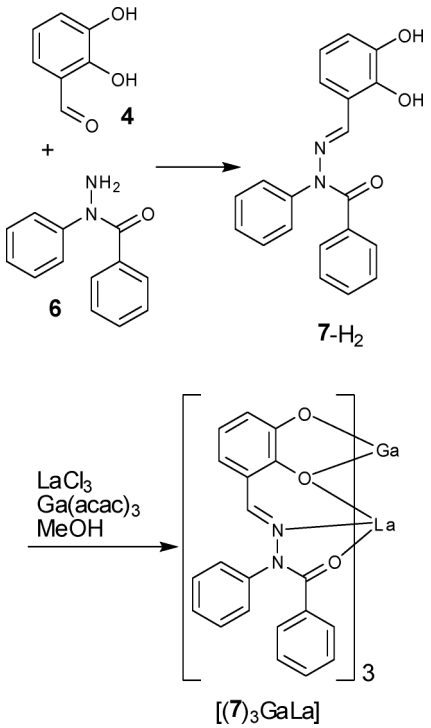


Fig. 2 Proton NMR spectra of $[(\mathbf{5b})_3GaLa]$ as well as of the free ligand **5b**-H_2 in DMSO-d_6.



Scheme 4 Preparation of the ligand **7**-H_2 and its heterodinuclear helicate $[(\mathbf{7})_3GaLa]$.

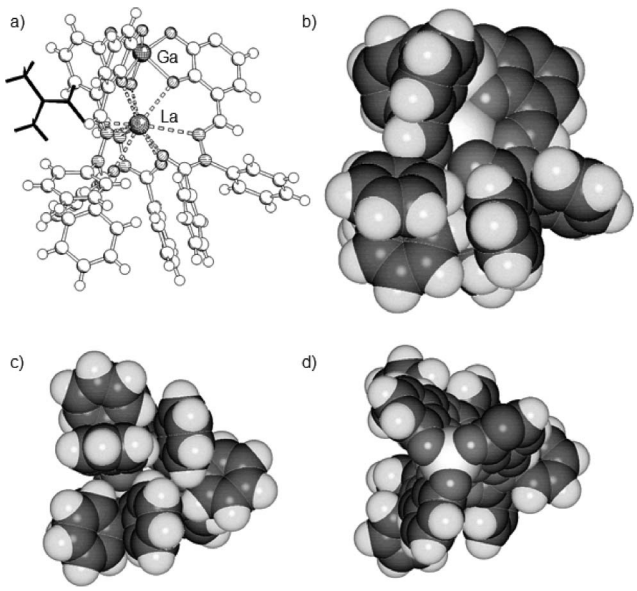


Fig. 3 Molecular structure of $[(\mathbf{7})_3GaLa]$ in the solid phase. Side view as ball and stick (a) as well as CPK model (b). Top view down the La-Ga (c) and the Ga-La axis (d). For clarity DMF is either only indicated (a) or omitted (b-d).

X-ray quality crystals of $[(\mathbf{7})_3GaLa]$ were obtained. In the crystal, one molecule of ether was observed as well as a dmf molecule, which coordinates to the lanthanum(III) ion. Fig. 3a shows the coordination environment at the gallium of $[(\mathbf{7})_3GaLa]$ which is bound by three catecholate units and at the lanthanum chelated by three acylhydrazones and additionally by the internal oxygen atoms of the catecholate units. Finally dmf is binding to the lanthanum(III) ion resulting in CN = 10 at this ion. Fig. 3b depicts a CPK model revealing the helical twist of the heterodinuclear complex. In addition, views down the La-Ga axis (c) as well as the Ga-La axis (d) are presented.

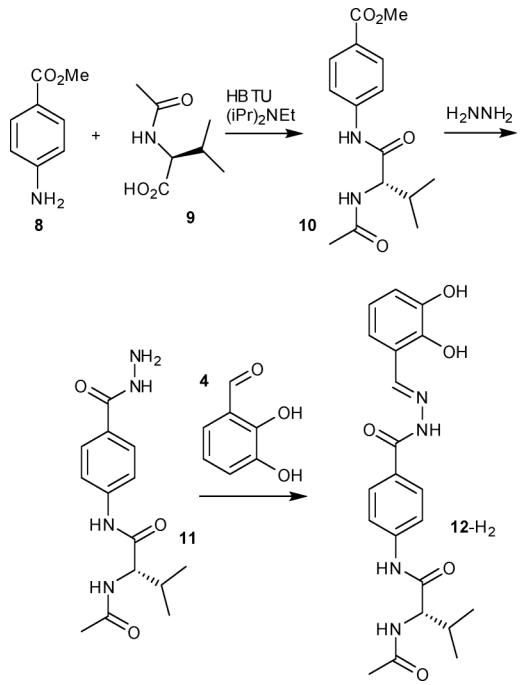
The structure of $[(\mathbf{7})_3GaLa]$·dmf is well comparable to the ones earlier described for complexes like **A** in which an NH is present instead of the N-Ph moiety. The three "new" phenyl substituents are located at the lower side of the complex ("lanthanide terminus") and are orientated towards the "outside". Now six phenyl groups are closely packed at this terminus of the helicate.

Amino acid functionalized ligands and complexes

The attachment of amino acid residues to the terminus of the heteroditopic ligands is of special interest. This might act as an anchor in order to attach peptidic chains. Metal coordination will preorganize three of the strands in order to generate interactions between amino acids (or peptides).[13]

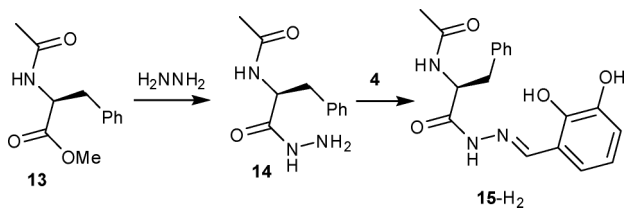
A first amino acid functionalized ligand was obtained starting from 4-amino benzoic acid methylester (**8**) and N-acyl valine (**9**). The benzoic ester **10** is formed in the presence of HBTU as amide coupling reagent. Reaction with hydrazine affords the acyl hydrazide **11**. Finally, ligand **12**-H_2 is obtained after hydrazone condensation of **11** with 2,3-dihydroxybenzaldehyde (**4**) (Scheme 5).

In ligand **12**-H_2 the amino acid is separated from the coordination side for the metals by the phenyl linker. **15**-H_2, on the other hand, represents a related compound in which the amino acid phenyl alanin is involved in the tridentate lanthanide binding side. This derivative is made from N-acyl phenylalanine



Scheme 5 Preparation of the ligand **12**-H_2.

methyl ester **13** by reaction with hydrazine. The resulting acyl hydrazide **14** forms the hydrazone **15**-H_2 by condensation with 2,3-dihydroxybenzaldehyde **4** (Scheme 6).



Scheme 6 Preparation of the ligand **15**-H_2.

Complexes of ligands **12**-H_2 and **15**-H_2 are synthesized by the standard method using three equivalents of the ligand, lanthanum(III) chloride and gallium tris(acetylacetonate) in the presence of potassium carbonate. For solubility reasons the heterodinuclear complexes $[(\mathbf{12})_3GaLa]$ and $[(\mathbf{15})_3GaLa]$ cannot be separated from the byproduct potassium chloride. However, the complexes can be well characterized by proton NMR, resulting in slightly broadened spectra which reveal one set of signals of the ligands. Most characteristic are the ESI MS spectra (Fig. 4). In the positive detection mode, peaks of the triple stranded heterodinuclear coordination compounds are observed at m/z = 1479 for $[K(\mathbf{12})_3GaLa]^+$ and at m/z = 1226 for $[H(\mathbf{15})_3GaLa]^+$.

The amino acid building blocks in ligands **12**-H_2 and **15**-H_2 were introduced as the naturally occurring S-isomer. Thus the ligands are obtained in enatiomerically pure form. The two compounds **12**-H_2 and **15**-H_2 as well as $[(\mathbf{12})_3GaLa]$ do not show significant CD signals. However, in case of $[(\mathbf{15})_3GaLa]$ strong negative Cotton effects are observed at 260, 330 nm and a slight negative effect at 370 nm. A strong positive Cotton effect is detected around 300 nm. This is tentatively interpreted by the ability of the phenyl alanine residue in **15** to induce the helical twist at the dinuclear metal complex. In $[(\mathbf{12})_3GaLa]$ the chiral units are too far away from the coordination sites and thus cannot influence the stereochemistry at the helicate unit.

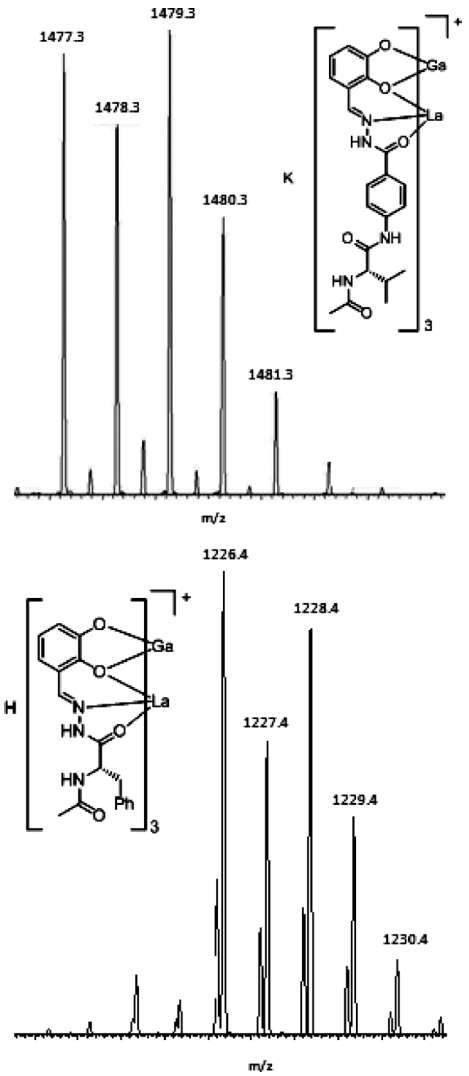


Fig. 4 Parts of the positive ESI MS spectra showing the molar peaks of $[K(\mathbf{12})_3GaLa]^+$ (top) and $[H(\mathbf{15})_3GaLa]^+$ (bottom).

Conclusions

In here the preparation of acylhydrazones of 2,3-dihydroxybenzaldehyde was presented, which act as ligands for the self-assembly of heterodinuclear lanthanide(III)-gallium(III) helicates. The new ligands are substituted at the acylhydrazone unit which binds the lanthanide ion. Three different types of ligands are presented: (1) Ligands **5a-c** possess alkyl chains of different length or benzyl groups located at the terminal phenyl unit. (2) Ligand **7** bears a phenyl group instead of the proton at the acyl hydrazone unit. (3) In compounds **12** and **15**, amino acid residues are attached to the lanthanide terminus of the ligand. All ligands nicely form the heterodinuclear metal complexes by simply mixing the metals (gallium(III) and lanthanum(III)) and ligands in correct stoichiometry.

For [(**7**)$_3$GaLa] an X-ray structural analysis could be obtained revealing the binding situation at the metal centers of the heterodinuclear complex. In case of [(**15**)$_3$GaLa] the helical twist at the heterodinuclear complex is induced by the chiral phenyl alanine residue.[14]

It has been demonstrated that the heteroditopic acylhydrazone ligands of 2,3-dihydroxybenzaldehyde easily can be functionalized at the "lanthanide terminus". This will be the motivation for future studies in order to introduce more sophisticated substituents (*e.g.* peptides) and to arrange them in space by metal directed self-assembly of heterodinuclear complexes.

Experimental Section

NMR spectra were recorded on a Varian Mercury 300 or Inova 400 spectrometer. FT-IR spectra were recorded on a Bruker IFS spectrometer. Mass spectra were taken on a Thermo Deca XP mass spectrometer. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyser. Compounds **3b,3c**[9] and **6**[12] were prepared following literature procedures.

The X-ray intensity data were collected in the ω scan mode on an Oxford Diffraction Xcalibur™2 diffractometer using graphite-monochromatized Mo-Kα radiation. The data were processed with CrysAlisPro.[15] They were corrected for Lorentz and polarization effects. Absorption corrections were carried out semi-empirically on the basis of multiple-scanned reflections.[16] The crystal structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97.[17] Due to the weak scattering power and the resulting low number of observed reflections anisotropic displacement parameters were introduced for all metal and oxygen atoms only. Hydrogen atoms were placed at geometrically calculated positions and refined with the appropriate riding model.

Syntheses

Synthesis of 2a. A mixture of 3,4,5-trihydroxymethylbenzoate (1 g, 5.39 mmol), propylbromide (2.22 g, 18.0 mmol) and an excess of K_2CO_3 (4.2 g, 30 mmol) solved in DMF (50 mL) was heated to 80 °C for 6 h. After cooling, the reaction was poured onto ice, extracted three times with 50 mL Et_2O and dried over $NaSO_4$. After filtration of the solid, the solvent was eliminated under reduced pressure. The product was purified by column chromatography (n-hexan/10% ethylacetate). The product was obtained as yellow oil in 84% yield (1.4 g, 4.5 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (s, 2H), 3.93 (t, 2H, *J* = 6.4 Hz), 3.91(t, 4H, *J* = 6.5 Hz), 3.83 (s, 3H), 1.85–1.68 (m, 6H), 0.98 (t, 6H, *J* = 7.4 Hz). - MS (EI, 70eV): *m/z* (%) = 310.3 (100%) $[M]^+$, 184.1 (65.4%) $[C_8H_5O_5]^+$. - IR (KBr): ν = 2917, 2849, 1716, 1587, 1504, 1468, 1431, 1336, 1224, 1128, 962, 763, 720 cm^{-1}. - $C_{17}H_{26}O_5$ (310.17): C 65.78, H 8.44; found C 65.86, H 8.73

Synthesis of 3a. To a methanolic solution of **2a** (0.16 g, 0.52 mmol), 20 mL hydrazine monohydrate were added drop wise under stirring and at room temperature within 15 min. After 24 h stirring the precipitate was filtered off, washed with water and dried under high vacuum. A white solid was obtained in 70% yield (0.112 g, 0.36 mmol). Melting point: 97–99 °C. - ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9,65 (br. s, 1H), 7.12 (s, 2H), 4.43 (br. s, 2H), 3.95 (t, 4H, *J* = 6.43 Hz), 3.87 (t, 2H, *J* = 6.31 Hz), 1.74 (hex, 4H, J = 7.18), 1.64 (hex, 2H, *J* = 7.18 Hz), 1.03–0.94 (m, 9H). - MS (EI, 70 eV): *m/z* (%) = 310.3 (24.9%) $[M]^+$, 279.2 (100%) $[C_{16}H_{23}O_4]^+$, 237.2 (52.8%) $[C_{13}H_{17}O_4]^+$. - IR (KBr): ν = 3264, 2963, 2877, 1629, 1584, 1495, 1427, 1341, 1242, 1118, 954, 761, 720 cm^{-1}. - $C_{17}H_{26}O_5$ (310.17): C 61.91, H 8.44, N 9.03; found C 62.23, H 8.44, N 8.51.

Synthesis of 5a. To a flask charged with a solution of **3a** (0.25 g, 0.81 mmol.) in MeOH (20 mL), 0.11 g (0.81 mmol) of **4** were added. The mixture was refluxed for 24 h. After cooling to 0 °C the precipitate was filtered off and washed with cold MeOH (10 mL). After drying under high vacuum the product was obtained as a grey solid in 52% yield (180 mg, 0.418 mmol). Melting point: 237 °C. - ^{1}H NMR (300 MHz, DMSO-d_6): δ = 11.90 (s, 1H), 11.12 (s, 1H), 9.22 (s, 1H), 8.60 (s, 6H), 7.23 (s, 2H), 6.97 (dd, 1H, *J* = 7.54 Hz, *J* = 1.61 Hz), 6.86 (d, 1H, *J* = 7.18 Hz), 6.75 (t, 1H, *J* = 7.79 Hz), 4.01 (t, 4H, *J* = 6.31 Hz), 3.92 (t, 2H, *J* = 6.31 Hz), 1.78 (hex, 4H, *J* = 6.97 Hz), 1.67 (hex, 2H, *J* = 6.93 Hz), 1.02 (t, 9H, *J* = 7.67 Hz). - MS (EI, 70 eV): *m/z* (%) = 430.3 (73%) $[M]^+$, 279.2 (100%) $[C_{16}H_{23}O_4]^+$, 237.2 (56.4%) $[C_{13}H_{16}O_4]^+$. - IR (KBr): ν = 3177, 2965, 2934, 1633, 1576, 1472, 1332, 1278, 1220, 1114, 956, 731 cm^{-1}. - $C_{17}H_{26}O_5$ (430.2): C 64.17, H 7.02, N 6.51; found: C 64.06, H 6.81, N 6.46

Synthesis of 5b. To a flask charged with a solution of **3b** (0.272 g, 0.77 mmol) in MeOH (20 mL), 0.138 g (1.00 mmol) of **4** were added. The mixture was refluxed for 24 h. After cooling to 0 °C precipitation occurred. The solid was filtered off and washed with cold MeOH (10 mL). After drying under high vacuum the product was obtained as a white solid in 48% yield (170 mg, 0.370 mmol). Melting point: 228–229 °C. - ^{1}H NMR(300 MHz, DMSO-d_6): δ = 11.90 (s, 1H), 11.12 (s, 1H), 9.22 (s, 1H), 8.60 (s, 6H), 7.23 (s, 2H), 6.97 (d, 1H, *J* = 7.67 Hz, *J* = 1.61 Hz), 6.86 (d, 1H, *J* = 7.66 Hz), 6.75 (t, 1H, *J* = 7.67 Hz), 4.05 (t, 4H, *J* = 6.31 Hz), 3.95 (t, 2H, *J* = 6.18 Hz), 1.75 (quin, 4H, *J* = 6.80 Hz), 1.67 (quin, 2H, *J* = 6.80 Hz), 1.54–1.40 (m, 6H),0.97 (t, 6H, *J* = 7.42 Hz), 0.92 (t, 9H, *J* = 7.30 Hz). - MS (EI, 70 eV): *m/z* (%) = 472.4 (53.0%) $[M]^+$, 321.3 (100%) $[C_{19}H_{29}O_4]^+$, 265.2 (63.9%) $[C_{15}H_{21}O_4]^+$, 153.1 (31.3%) $[C_7H_5O_4]^+$. - IR (KBr): ν = 3484, 2959, 2934, 2873, 1642, 1581, 1558, 1330, 1197, 1108, 958, 727 cm^{-1}. - $C_{49}H_{92}O_4N_2 \cdot 0.33\ CH_3OH$: C 65.45, H 7.79 N, 5.86; found: C 65.39, H 7.38, N 5.83.

Synthesis of 5c. To a solution of **3e** (0.091 g, 0.2 mmol) in MeOH (20 mL), 0.036 g (0.26 mmol) of **4** were added. The mixture was refluxed for 24 h. After cooling to 0 °C a precipitate was formed, which was filtered and washed with cold MeOH (10 mL). After drying under high vacuum the product was obtained as a grey solid in 86% yield (100 mg, 0.174 mmol). Melting point: 136–138 °C. - ^{1}H NMR (300 MHz, DMSO-d_6): δ = 11.95 (s, 1H), 11.05 (s, 1H), 9.23 (s, 1H),8.62 (s, 6H), 7.53–7.36 (m, 17H), 6.99 (dd, 1H, *J* = 7.67 Hz, *J* = 1.48 Hz), 6.87 (dd, 1H, *J* = 7.92 Hz, *J* = 1.49 Hz), 6.75 (t, 1H, *J* = 7.79 Hz), 5.22 (s, 4H),5.04 (s, 2H). - MS (EI, 70 eV): *m/z* (%) = 574.4 (19%) $[M]^+$, 91.1 (100%) $[C_7H_7]^+$. - IR (KBr): ν = 3436, 3247, 1580, 1501, 1334, 1222, 1122, 970, 965, 730 cm^{-1}.

General procedure for the preparation of the complexes

To a solution of one of the ligands **5a**-H_2 to **5c**-H_2 (3.0 equiv.) in MeOH (25 mL), 3.0 equiv. of K_2CO_3 were added. A yellowish solution formed. 3.0 equiv. of $LaCl_3 \cdot 7H_20$ as well as $Ga(acac)_3$

were added. The mixture was stirred over night. The product was filtered off and washed with MeOH and Et_2O.

[(5a)$_3$GaLa]. Yield: 0.040 g (91%). - ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 12.43 (s, 1H), 8.40 (s, 1H), 7.10 (s, 2H), 6.40 (br.s, 3H), 3.88 (br.s, 2H), 3.57 (br.s, 2H), 3.38 (br.s, 2H), 1.66–1.44 (m, 6H), 0.95(t, 3H, J = 7.54 Hz), 0.89 (t, 6H, J = 7.54 Hz). - MS (ESI-): m/z (%) = 1650.88 (100%) ([LaGa[**5a**]$_3$+CH$_3$O)$^-$. - IR (KBr): ν = 2966, 2938, 1604, 1567, 1454, 1253, 1217, 1118, 737 cm^{-1}. - $C_{69}H_{84}GaLaN_6O_{18}\cdot 3\ H_2O$: C 53.53, H 5.68, N 5.43; found: C 53.47, H 5.63, N 5.44.

[(5b)$_3$GaLa]. Yield: 0.042 g (90%). - ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 12.45 (s, 1H), 8.40 (s, 1H), 7.10 (s, 2H), 6.32–6.48 (m, 3H), 3.88 (t, 2H, J = 7.45 Hz), 3.60 (br.s, 2H), 3.41 (br.s, 2H), 1.63–1.30 (m, 12H), 0.90 (t, 3H, J = 7.42 Hz), 0.87 (t, 6H, J = 7.17 Hz). - MS (ESI-): m/z (%) = 1491.33 (80%) ([LaGa[**5b**]$_3$-H)$^-$, 925.33(100%)[Ga[**5b**]]$^-$ - IR (KBr): ν = 2958, 2934, 2872, 1600, 1566, 1497, 1453, 1427, 1375, 1337, 1253, 1215, 1105, 1059, 864, 736 cm^{-1}. - $C_{78}H_{102}GaLaN_6O_{18}\cdot 3\ H_2O$: C 55.95, H 6.50, N 5.02; found: C 55.85, H 6.39, N 5.01.

[(5c)$_3$GaLa]. Yield: 0.013 g (81%). - ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 12.43 (s, 1H), 8.49 (s, 1H), 7.43–7.08 (m, 17H), 6.46–6.41 (m, 3H), 4.78 (br.s, 2H), 4.60 (br.s, 2H), 3.20 (br.s, 2H). - IR (KBr): ν = 3032, 1567, 1452, 1371, 1337, 1250, 1215, 1103, 973, 847, 823, 733, 694 cm^{-1}. - $C_{105}H_{84}GaLaN_6O_{18}\cdot 12\ H_2O$: C 58.86, H 5.08, N 3.92; found: C 58.27, H 4.10, N 3.85.

Synthesis of 7-H$_2$. A mixture of N′-phenylbenzhydrazine **6** (550 mg, 2.6 mmol) and 2,3-dihydroxybenzaldehyde **4** (280 mg, 2.0 mmol; 1 eq) was dissolved in 10 mL $CHCl_3$. The mixture was heated to reflux for 7 h and then was stirred over night. After recrystallization from 15 mL $CHCl_3$ the product was dried under vacuum. A brown solid was obtained in quantitative yield (684 mg, 2.0 mmol). Melting point: 170 °C. - ^{1}H NMR (400 MHz, 25 °C, CD_3OD): δ = 7.88 (s, 1 H), 7.68 (d, J = 8.0 Hz, 2 H), 7.62 (t, J = 7.4 Hz, 1 H), 7.56–7.44 (m, 4 H), 7.39 (m, 3 H), 6.77 (d, J = 7.5 Hz, 1 H), 6.65 (t, J = 7.7 Hz, 1H), 6.62 (dd, J = 7.7 Hz, 1 H). - MS (EI, 70 eV): m/z (%) = 332.1 (6.24) [M]$^+$, 105.1 (100) [C_7H_5O]$^+$, 77.2 (44.88) [C_6H_5]$^+$. - IR (KBr): ν = 3351, 3024, 2322, 2079, 1631, 1489, 1410, 1340, 1259, 1211, 1026, 842, 747, 696 cm^{-1}. - $C_{20}H_{16}N_2O_3\cdot CHCl_3$: C 55.84, H 3.79, N 6.20; found: C 55.72, H 3.94, N 6.36.

[(7)$_3$GaLa]. Ligand **7**-H$_2$ (70 mg, 0.2 mmol), K_2CO_3 (15 mg, 0.105 mmol), $LaCl_3\cdot 7H_2O$ (26 mg, 0.07 mmol) and Ga(acac)$_3$ (25 mg, 0.07 mmol; 1 Äq) were dissolved in 8 mL MeOH and the mixture was stirred for 12 h at RT. A yellow solid precipitated, which was filtered off, washed with MeOH and dried under high vacuum. The product was obtained in 50% yield (42 mg, 0.035 mmol). ^{1}H NMR (300 MHz, 25 °C, DMSO-d$_6$): 7.84 (s, 1H), 7.45 (m, 5 H), 6.98 (t, J = 7.4 Hz, 1 H), 6.76 (d, 2H, J = 7.4 Hz), 6.50 (d, 2H, J = 7.4 Hz), 6.38 (t, 1H, J = 7.67 Hz), 6.08 (m, 2H). - positive ESI MS: m/z (%) = 1199.33 (100%) [LaGa[**6**]$_3$+H]$^+$.- IR (KBr): ν = 3666, 3349, 3060, 2745, 2321, 2079, 1567, 1545, 1451, 1424, 1369, 1262, 1209, 1013, 872, 768, 729, 697, 660 cm^{-1}.- $C_{60}H_{42}N_6O_9GaLa\cdot 2H_2O$: C 58.32, H 3.75, N 6.80, found: C 57.89, H 3.46, N 6.76.

Crystal data. [(**7**)$_3$GaLa]: $C_{67}H_{59}N_7O_{11}GaLa$: formula weight 1346.84, monoclinic, space group $P2_1/n$, a = 15.864(3), b = 23.356(3), c = 17.036(2) Å, β = 104.622(14)°, V = 6107.5(16) Å^3, Z = 4, T = 110(2)K, Mo-Kα, ρ = 1.465 g cm^3,μ = 1.199 mm^{-1}, 41590 collected data, 9287 unique reflections (θ_{max} = 23.75°), R_{int} = 0.1135, 3360 observed reflections [$I > 2\sigma(I)$], GOF = 0.606, R1 [I > 2s(I)] = 0.0406, wR_2 (all data) = 0.0601. Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 789894.† Copies of the data can be obtained free of charge on application to CHGC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or E-Mail: deposit@ccdc.cam.ac.uk).

Synthesis of 10. *N*-Acyl-L-valine **9** (330 mg, 2.07 mmol) was dissolved in 15 mL DMF. EDC (448 m, 2.34 mmol) and HOBt (316 mg, 2.34 mmol) were added to the solution. After stirring of the mixture for 30 min, a solution of 4-aminomethylbenzoate **8** (469 mg, 3.10 mmol) in 10 mL DMF was added. The mixture was stirred for 4 days at room temperature. After that the solvent was removed under high vacuum and the rest was dissolved in DCM, washed with NH_4Cl, $NaHCO_3$, H_2O and brine, dried with Na_2SO_4 and solvent was removed using rotary evaporation. The product was purified by column chromatography DCM/MeOH (10 : 1). A white solid was obtained in 38% yield (239 mg, 0.79 mmol). Melting point: 200–202 °C. - ^{1}H NMR (300 MHz, CD_3OD-d$_4$): δ = 7.85 (d, 2H, J = 8.66 Hz), 7.60 (d, 2H, J = 8.66 Hz), 6.54 (d, 1H, J = 8.41 Hz), 2.02 (sept, 1H, J = 6.92 Hz), 1.92 (s, 3H), 0.92 (d, 6H, J = 6.68 Hz). - MS (EI,70eV): m/z (%) = 292.3 (2.09%) [M]$^+$, 190.2 (1.12%) [$C_{11}H_{12}NO_2$]$^+$, 151.2 (53.53%) [$C_8H_8NO_2$]$^+$, 120.2 (25.07%) [$C_5H_7NO_2$]$^+$, 114.2 (40.04%) [$C_6H_{12}NO$]$^+$. - IR (KBr): ν = 3308, 3117, 3017, 2965, 2850, 2433, 1925, 1713, 1652, 1602, 1538, 1436, 1410, 1381, 1283, 1175, 1111, 1016, 966, 927, 856, 758, 698, 667, 599, 513 cm^{-1}. - HRMS calculated for $C_{15}H_{20}O_4Na$: 315.13174 found: 315.13153.

Synthesis of 11. To a methanolic solution of 4-(amino(S)-*N*-acylvaline) methylbenzoate **10** (90 mg, 0.31 mmol), 0.5 mL $NH_2NH_2\cdot H_2O$ were added. The mixture was heated to reflux for 48 h. The solvent was removed under rotary evaporation and the product was recrystallized from MeOH/Et_2O. A white solid was obtained in 70% yield (63 mg, 0.22 mmol). Melting point: 215.9–217.6 °C. - ^{1}H NMR (300 MHz, CD_3OD): δ = 7.76 (d, 2H, J = 8.90 Hz), 7.69 (d, 2H, J = 8.90 Hz), 4.29 (d, 1H, J = 7.67 Hz), 2.05 (m, 1H), 1.98 (s, 3H), 1.02 (d, 6H, J = 6.68 Hz). - MS (EI,70eV): m/z (%) = 292.3 (0.83%) [M]$^+$, 261.3 (7.59%) [$C_{14}H_{17}N_2O_3$]$^+$, 151.2 (19.90%) [$C_8H_8NO_2$]$^+$, 120.2 (100.00%) [$C_5H_7NO_2$]$^+$. - IR (KBr): ν = 3842, 3283, 2961, 2707, 2421, 2284, 2421, 2284, 2166, 2076, 1992, 1918, 1776, 1634, 1525, 1439, 1405, 1380, 1333, 1252, 1196, 1113, 962, 849, 762, 718, 670 cm^{-1}.- $C_{14}H_{20}N_4O_3\cdot H_2O$ (292.1): C 54.18 H 7.15 N 18.05; found C 52.82 H 6.78 N 18.35; HRMS calculated for $C_{14}H_{20}O_3Na$: 315.14276 found: 315.14240.

Synthesis of 12-H$_2$. To a methanolic solution of 4-(amino(S)-*N*-acylvaline) methylbenzohydrazid **11** (160 mg, 0.55 mmol), a methanolic solution of 2,3-dihydroxybenzaldehyde **4** (76 mg, 0.55 mmol) was added. The mixture was stirred for 24 h at room temperature. The solvent was removed under rotary evaporation and the product was recrystallized from MeOH/Et_2O. A grey solid was obtained in 64% yield (143 mg, 0.35 mmol). Melting point: 270.8–273.7 °C. - ^{1}H NMR (300 MHz, CD_3OD): δ = 8.45 (s, 1H), 7.92 (d, 2H, J = 8.17 Hz), 7.78 (d, 2H, J = 8.17 Hz), 6.88 (m, 2H), 6.79 (t, 1H, J = 7.66 Hz), 4.29 (d, 1H, J = 7.67 Hz),

2.10 (m, 1H), 1.98 (s, 3H), 1.02 (2 s, 6H). - MS (EI,70eV): *m/z* (%) = 412.2 (15.11%) $[M]^+$, 261.2 (19.31%) $[C_{14}H_{17}N_2O_3]^+$, 136.1 (68.40%) $[C_7H_6NO_2]^+$, 120.1 (100.00%) $[C_5H_7NO_2]^+$. - IR (KBr): ν = 3844, 3612, 3487, 3377, 3285, 3054, 2966, 2933, 2876, 2696, 2473, 2321, 2288, 2163, 2058, 1971, 1942, 1923, 1859, 1744, 1688, 1602,1531, 1468, 1409, 1367, 1310, 1185, 1100, 1062, 1018, 902, 851, 783, 761, 731, 686, 659 cm^{-1}. - $C_{21}H_{24}N_4O_5$ (412.2): C 61.15 H 5.87 N 13.58; found C 60.81 H 5.05 N 11.58.

[(12)$_3$GaLa]. Ligand **12**-H_2 (22 mg, 0.053 mmol), K_2CO_3 (5 mg, 0.027 mmol), $LaCl_3{\cdot}7H_2O$ (6.6 mg, 0.017 mmol) and $Ga(acac)_3$ (6 mg, 0.017 mmol) were dissolved in 10 mL DMF and the mixture was stirred for 24 h at RT. Precipitated salt was filtered off and DMF was removed under high vacuum. The product was obtained as yellow solid in 82% yield (20 mg, 0.014 mmol). ^{1}H NMR (400 MHz, 25 °C, CD_3OD): δ = 8.67 (s, 1H), 7.94 (d, 2H, *J* = 8.9 Hz), 7.58 (d, 2H, *J* = 8.9 Hz), 6.82 (d, 1H, *J* = 7.7 Hz), 6.75(d, 1H, *J* = 7.7 Hz), 6.50 (t, 1H, *J* = 7.7 Hz), 4.29 (d, 1H, *J* = 7.7 Hz), 2.10 (m, 1H), 2.00 (s, 3H), 0.98 (2 s, 6H). - positive ESI MS: *m/z* (%) = 1477.3 $[(\mathbf{12})_3LaGaK]^+$. - IR (KBr): ν = 3850, 3304, 3055, 2967, 2874, 2659, 2321, 2169, 2105, 1997, 1734, 1658, 1602, 1517, 1450, 1376, 1251, 1164, 1035, 855, 745, 686 cm^{-1}. - $C_{63}H_{66}N_{12}O_{15}GaLa{\cdot}4$ KCl: C 43.54, H 3.83, N 9.67, found: C 43.40, H 3.98, N 9.59.

Synthesis of 14. To a methanolic solution of N-acyl-L-phenylalanine methylester **13** (286 mg, 1.21 mmol), 0.2 mL of hydrazinmonohydrate (2.64 mmol) were added and the solution was stirred at RT for 2 days. The solvent was removed under high vacuum. A white solid was obtained in quantitative yield (286 mg, 1.21 mmol). Melting point: 177.3–178.3 °C. - ^{1}H NMR (400 MHz, CD_3OD): δ = 7.13 (m, 5H), 4.45 (dd, 1H, *J* = 8.6, 2.0 Hz), 2.97 (dd, 1H, J = 13.6 6.6 Hz), 2.77 (dd, 1H, *J* = 13.6, 8.62 Hz), 1.79 (s, 3H). - MS (EI, 70eV): *m/z* (%) = 222.1 (2.22%) $[M+H]^+$, 190.1 (54.60%) $[C_{11}H_{12}NO_2]^+$, 120.1 (100%) $[C_5H_7NO_2]^+$. - IR (KBr): ν = 3299, 3034, 2322, 1740, 1636, 1531,1374, 1292, 1254, 1103, 1035, 939, 750, 699, 667 cm^{-1}. - $C_{11}H_{15}N_3O_2$ (221.1): C 59.71, H 6.83, N 18.99; found C 59.41, H 6.12, N 18.87.

Synthesis of 15-H_2. A mixture of N-acetyl-L-phenylalaninehydrazide **14** (100 mg, 0.4253 mmol) and 2,3-dihydroxybenzaldehyde **4** (59 mg, 0.4253 mmol) were dissolved in 15 mL MeOH and heated to reflux for 7 h. After that the solvent was removed and the product was recrystallized from 5 mL MeOH/Et_2O (1 : 3). A light yellow solid was obtained in 70% yield (101 mg, 0.30 mmol). Melting point: 211.4–214 °C. - ^{1}H NMR (300 MHz, CD_3OD): δ = 8.16 (s, 1H), 7.25 (m,5H), 6.85 (dd, 1H, *J* = 7.7, 1.7 Hz), 6.80 (dd, 1H, *J* = 7.7, 1.7 Hz), 6.72 (t, 1H, *J* = 7.7 Hz), 4.65 (t, 1H, *J* = 7.2 Hz), 3.15 (dd, 1H, *J* = 13.6, 7.2 Hz), 2.97 (dd, 1H, *J* = 13.6, 7.2 Hz), 1.93 (s, 3H). - MS (EI,70eV): *m/z* (%) = 341.1 (5.60%) $[M]^+$, 190.1 (49.09%) $[C_{11}H_{12}NO_2]^+$, 120.2 (100%) $[C_5H_7NO_2]^+$. - IR (KBr): ν = 3520, 3264, 3061, 2925, 2857, 2738, 2319, 2113, 1756, 1649,1540, 1470, 1362, 1266, 1064, 1038, 958, 845, 782, 731, 697 cm^{-1}. - $C_{18}H_{19}N_3O_4{\cdot}H_2O$ (341.1): C 60.16, H 5.89, N 11.69; found C 60.68, H 5.90, N 12.19.

[(15)$_3$GaLa]. Ligand **15**-H_2 (30 mg, 0.088 mmol), K_2CO_3 (15 mg, 0.105 mmol), $LaCl_3{\cdot}7H_2O$ (11 mg, 0.029 mmol) and $Ga(acac)_3$ (10.7 mg, 0.029 mmol) were dissolved in 10 mL DMF and the mixture was stirred for 48 h at RT. Salts were filtered off and DMF was removed under high vacuum. The product was obtained as an orange solid in 84% yield (30 mg, 0.024 mmol). ^{1}H NMR (300 MHz, 25 °C, CD_3OD): δ = 8.19 (s, 1H), 7.2 (m, 5 H, CHPh) 6.90 (d, *J* = 8.7 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 1H), 6.40 (d, *J* = 8.7 Hz, 1H), 4.60 (s, 1H), 3.07 (m, 2H), 1.89 (s, 3H). - positive ESI MS: *m/z* (%) = 1226.53 (50%) $[LaGa(\mathbf{15})_3+H]^+$.- IR (KBr): ν = 3225, 3030, 2927, 2810, 2616, 2453, 2321, 2231, 2202, 2105, 2051, 1992, 1957, 1886, 1601, 1551, 1453, 1375, 1254, 1216, 1056, 959, 867, 785, 742, 699 cm^{-1}. - $C_{54}H_{51}N_9O_{12}GaLa{\cdot}4H_2O{\cdot}7$ KCl: C 35.62, H 3.27, N 6.92, found: C 35.87, H 3.31, N 6.73.

Acknowledgements

This work was supported by the Fonds der Chemischen Industrie (MA).

Notes and references

1 (*a*) J.-M. Lehn, *Supramolecular Chemistry - Concepts and Perspectives*, VCH,Weinheim, 1995; (*b*) D. Philpand and J. F. Stoddart, *Angew. Chem.*, 1996, **108**, 1243, (*Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1154); (*c*) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; (*d*) B. Olenyuk, A. Fechtenkötter and P. J. Stang, *J. Chem. Soc., Dalton Trans.*, 1998, 1707.

2 (*a*) R. W. Saalfrank, A. Stark, K. Peters and H. G. von Schnering, *Angew. Chem.*, 1988, **100**, 878, (*Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 851); (*b*) E. J. Enemark and T. D. P. Stack, *Angew. Chem.*, 1998, **110**, 977, (*Angew. Chem., Int. Ed.*, 1998, **37**, 932); (*c*) M. Scherer, D. L. Caulder, D. W. Johnson and K. N. Raymond, *Angew. Chem.*, 1999, **111**, 1690, (*Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 1588).

3 E.g. (*a*) X. Sun, W. J. Darren, D. Caulder, R. E. Powers, K. N. Raymond and E. H. Wong, *Angew. Chem.*, 1999, **111**, 1386–1390, (*Angew. Chem., Int. Ed.*, 1999, **38**, 1303); (*b*) X. Sun, D. W. Johnson, D. Caulder, K. N. Raymond and E. H. Wong, *J. Am. Chem. Soc.*, 2001, **123**, 2752–2763; (*c*) A. K. Das, A. Rueda, L. R. Falvello, S.-M. Peng and S. Batthacharya, *Inorg. Chem.*, 1999, **38**, 4365–4368; (*d*) J. Heinicke, N. Peulecke, K. Karaghiosoff and P. Mayer, *Inorg. Chem.*, 2005, **44**, 2137–2139; (*e*) M. D. Ward, *Coord. Chem. Rev.*, 2007, **251**, 1663–1677.

4 Reviews: (*a*) E. C. Constable, *Tetrahedron*, 1992, **48**, 10013–10059; (*b*) C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005–2062; (*c*) M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457–3498; (*d*) M. J. Hannon and L. J. Childs, *Supramol. Chem.*, 2003, **16**, 7–22; (*e*) M. Albrecht, I. Janser and R. Fröhlich, *Chem. Commun.*, 2005, 157–165 see also; (*f*) R. W. Saalfrank and B. Demleitner, in *Transition Metals in Supramolecular Chemistry*J.-P. Sauvage, Ed.; John Wiley & Sons, New York, 1999; Vol. 5, pp 1-51; (*g*) R. W. Saalfrank, H. Maid and A. Scheurer, *Angew. Chem.*, 2008, **120**, 8924–8956, (*Angew. Chem., Int. Ed.*, 2008, **47**, 8794).

5 (*a*) C. Piguet, G. Hopfgartner, B. Bocquet, O. Schaad and A. F. Williams, *J. Am. Chem. Soc.*, 1994, **116**, 9092–9102; (*b*) C. Piguet, G. Bernardinelli, J.-C. G. Bünzli, S. Petoud and G. Hopfgartner, *Chem. Commun.*, 1995, 2575–2577; (*c*) M. Albrecht and R. Fröhlich, *J. Am. Chem. Soc.*, 1997, **119**, 1656–1661; (*d*) F. E. Hahn, M. Offermann, C. Schulze Isfort, T. Pape and R. Fröhlich, *Angew. Chem.*, 2008, **120**, 6899–6902, (*Angew. Chem., Int. Ed.*, 2008, **47**, 6794); (*e*) M. Albrecht, O. Osetska, R. Fröhlich, J.-C. G. Bünzli, A. Aebischer, F. Gumy and J. Hamacek, *J. Am. Chem. Soc.*, 2007, **129**, 14178–14179; (*f*) M. Albrecht, O. Osetska, J.-C. Bünzli, F. Gumy and R. Fröhlich, *Chem.–Eur. J.*, 2009, **15**, 8791–8799for more recent work see; (*g*) E. Terazzi, L. Guenee, J. Varin, B. Bocquet, J.-F. Lemonnier, D. Emery, J. Mareda and C. Piguet, *Chem.–Eur. J.*, 2011, **17**, 184–195.

6 M. Albrecht, Y. Liu, S. S. Zhu, C. A. Schalley and R. Fröhlich, *Chem. Commun.*, 2009, 1195–1197.

7 M. Albrecht, I. Latorre, Y. Liu and R. Fröhlich, *Z. Naturforsch B*, 2010, **65B**, 311–316.

8 K. Dodo, T. Minato, T. Noguchi-Yachide, M. Suganuma and Y. Hashimoto, *Bioorg. Med. Chem.*, 2008, **17**, 7975–7982.

9 M. Li and S. Qu, *Tetrahedron*, 2007, **63**, 12429–12436.

10 E.g. (*a*) P. Melnyk, V. Leroux, C. Sergheraert and P. Grellier, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 31–35; (*b*) O. Pouralimardan, A.-C. Chamayou, C. Janiak and H. Hosseini-Monfared, *Inorg. Chim. Acta*,

2007, **360**, 1599–1608. For related semicarbazone derived ligands and their mononuclear complexes, see; (*c*) M. Albrecht, O. Osetska and R. Fröhlich, *Dalton Trans.*, 2005, 3757–3762; (*d*) M. Albrecht, S. Mirtschin, O. Osetska, S. Dehn, D. Enders, R. Fröhlich, T. Pape and F. E. Hahn, *Eur. J. Inorg. Chem.*, 2007, 3276–3287.
11 E.g. M. Albrecht, M. Baumert, H. D. F. Winkler, C. A. Schalley and R. Fröhlich, *Dalton Trans.*, 2010, **39**, 7220–7222.
12 R. Yamasaki, A. Tanatani, I. Azumaya, H. Masu, K. Yamaguchi and H. Kagechika, *Cryst. Growth Des.*, 2006, **6**, 2007–2010.
13 M. Albrecht and P. Stortz, *Chem. Soc. Rev.*, 2005, **34**, 496–506.
14 For chiral induction of terminal substituents on helicates, see *e.g.* M. Albrecht, *Synlett*, 1996, 565.
15 *CrysAlisPro Version 1.171.33.41*, Oxford Diffraction Ltd, Yarnton, Oxfordshire, UK.
16 R. H. Blessing, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1995, **A 51**, 33.
17 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **A 64**, 112.

