The Synthesis of Catechol and 8-Hydroxyquinoline Derivatives with Short Peptide-Type Side Chains: Metal Complex Ligands with Additional Receptor Properties

Markus Albrecht,*[a] Jeanette Zauner,[a] Thomas Eisele,[a] Patrick Weis[b]

[a] Institut für Organische Chemie, RWTH-Aachen, Prof.-Pirlet-Str. 1, 52074 Aachen, Germany
Fax +49(241)8092385; E-mail: markus.albrecht@oc.rwth-aachen.de

[b] Institut für Physikalische Chemie, Universität Karlsruhe, Fritz-Haber-Weg, 76128 Karlsruhe, Germany

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Abstract: Glycine-*N*-amide substituted catechol and 8-hydroxyquinoline ligands were prepared and were used to obtain mixtures of isomers of dicatecholate molybdenum(VI)dioxo and tris-8-hydroxyquinolinate gallium(III) complexes. Upon addition of nitrate to the complex $[(\mathbf{5})_2MoO_2]^{2-}$ an allosteric binding of the metal as well as of the anion takes place.

Key words: allosteric effects, ligand, amide, metal complex, receptors

Recognition processes between receptors and substrates play an essential role in biological systems. To gain some understanding for such processes, it is of interest to investigate into artificial molecules which are able to bind molecular guests. Hereby the interaction between receptor and substrate proceeds by non-covalent interactions due to favorable geometries and to complementary electronic features of the molecular species ('lock-and-key principle').[1]

Hydrogen bonding is one of the most common non-covalent binding motifs found in nature. This weak interaction allows a reversible binding of guests and ideally shows high selectivity towards different molecular species. As model systems, tweezer-type compounds with functionalized side-arms were investigated during the last 20 to 30 years and their receptor ability towards different guests was studied.[2–8]

Recently, we started to investigate tweezer-type compounds composed of a biphenol, a catechol, or a resorcinol backbone and two glycine-*N*-amide (or urea) based side-arms. Due to the hydrogen bond donor/acceptor units in the side arms the molecules are able to bind nitrate as a planar anionic guest.[9,10]

In the present paper we describe the synthesis of derivatives which on the one hand form metal complexes, on the other hand bear side chains based on amino acids or short peptidic units. Those functionalities by hydrogen bonding can interact with guest species.[11] In a preliminary study we demonstrate that an allosteric effect can take place between the strong non-covalent binding of the metal ion and the relatively weak interaction with nitrate as an anionic guest (Figure 1).

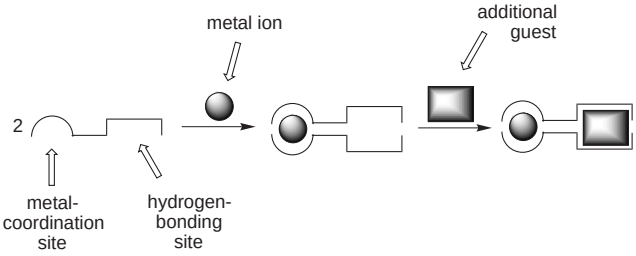

Figure 1 Schematic representation of a ditopic ligand with the ability to bind one metal ion and one additional guest species

The glycine-*N*-amide (or urea) substituted catechols and 8-hydroxyquinolines are prepared starting from the amines 2,3-dimethoxybenzyl amine (**1**), 7-amino-8-hydroxyquinoline (**8a**)[12,13] and 7-aminomethyl-8-hydroxyquinoline (**8b**)[14] by attaching the glycine side chains through amide linkages.[15]

Therefore, the glycine-*N*-amides **2a** and **2b** have to be prepared first. Reaction of glycine with laurinic acid chloride (dodecanoylchloride) or benzoic acid chloride in the presence of sodium hydroxide leads to the glycine derivatives **2a** (45%) and **2b** (41%), respectively. Hereby the long alkyl chain is introduced to solubilize the envisaged coordination compounds in non-polar solvents, in which host/guest interactions with the additional guest will be studied.

The thus prepared compounds **2a** and **2b** and the commercially available *N*-BOC protected glycine **2c** are activated by reaction with HBTU in the presence of Hünig's base $[EtN(i\text{-}Pr)_2]$[16,17] and in situ 2,3-dimethoxybenzyl amine (**1**) is added to obtain after work up the desired amides in 74% (**3a**), 82% (**3b**) or 88% yield (**3c**) (Scheme 1).

The urea derivative **4** is prepared starting from **3c** by cleavage of the BOC protecting group with HCl in dry ether. The intermediate hydrochloride of the amine is not characterized but subsequently reacted with octadecyl isocyanate in acetonitrile to form **4** in 83% yield (Scheme 1). During the latter reaction step it is important to add some base for the deliberation of the amine. *N*-Methylmorpholine proved to be the most appropriate base for this purpose.[18] The use of less hindered (more nucleophilic) bases led to an undesired cyclization side reaction.

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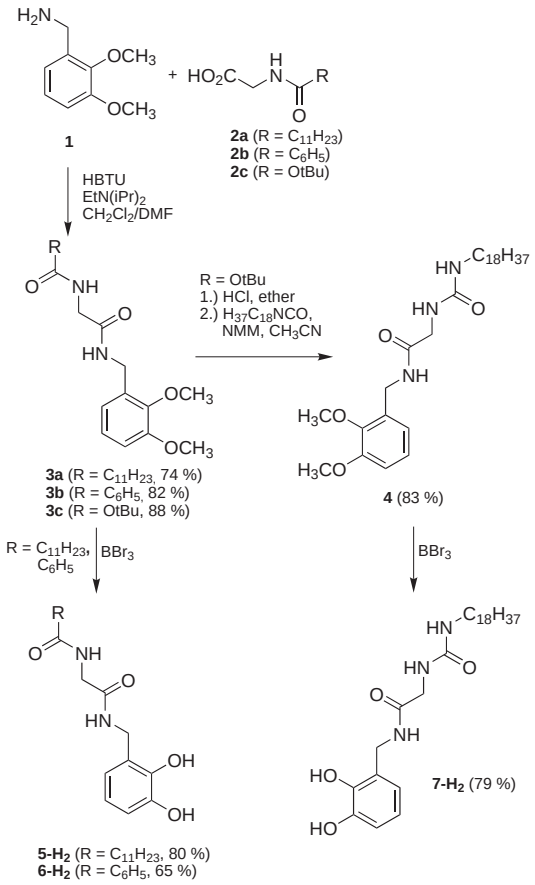
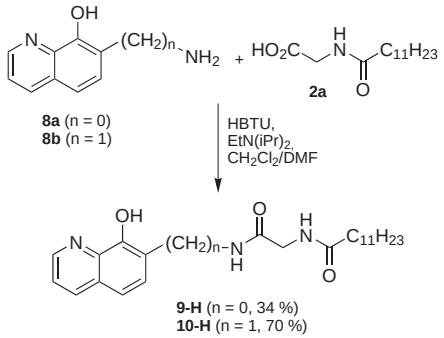


Scheme 1

Finally the methyl ethers of **3a**, **3b** and **4** are cleaved by reaction with BBr_3 in dichloromethane to obtain the catechol ligands **5**-H_2 (80%), **6**-H_2 (65%) and **7**-H_2 (79%). To remove traces of boron the oily compounds in water are treated with sonic sound and the pure catechol derivatives precipitate as white solids.



Scheme 2

The synthesis of the 8-hydroxyquinoline derivatives **9-H** and **10-H** starts with the amines **8a** and **8b** which were prepared by literature procedures.[12–14] Again the acid moiety of **2a** is activated by reaction with HBTU in the presence of Hünig's base and then is coupled with either 7-amino-8-hydroxyquinoline (**8a**) or 7-aminomethyl-8-hydroxyquinoline (**8b**). The hydroxyquinolines are obtained in 34% (**9-H**) and 70% yield (**10-H**). Hereby the yield of **9-H** is low due to the fact that only the precipitated pure product was isolated; some material still stayed in solution. Compound **10-H** is purified by recrystallization from chloroform (Scheme 2).

With the catechol and the 8-hydroxyquinoline derivatives in hand we are able to investigate the coordination chemistry of those compounds as well as in the receptor behavior of their metal complexes.

Catechol and its derivatives form 2:1 complexes with the molybdenum(VI)dioxo unit and therefore should be ideal for the formation of tweezer-type complexes with two side arms present. In 1997 Prévot-Halter, Smith and Weiss[19] used pyridineamide substituted catechols as ligands for molybdenum(VI)dioxide and they could show that one of the isomers of coordination compounds is able to bind dicarboxylic acids. Upon binding of the diacid the composition of the mixture of isomers was shifted towards the component with the highest affinity for the acid.[19]

Molybdenum(VI)dioxo complexes of the catechol ligands **5**–**7** are obtained by reaction of two equivalents of the ligand with one equivalent of $MoO_2(acac)_2$ in the presence of potassium carbonate in methanol.[20–24] The crude product which is obtained after removal of the solvent is purified by chromatography over lipophilic Sephadex LH 20 (Figure 2).

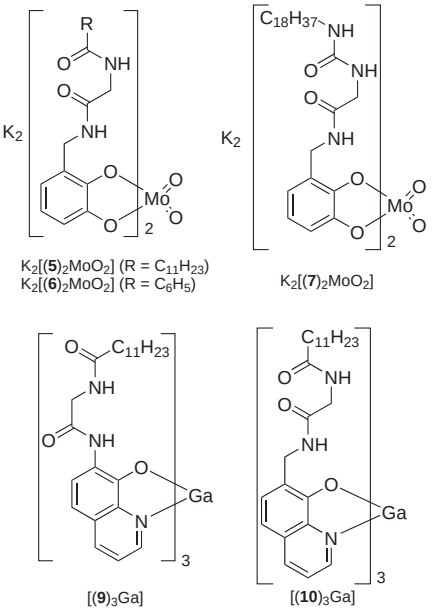


Figure 2 Complexes which are described in this study

NMR spectroscopy of the coordination compounds $K_2[(\mathbf{5}–\mathbf{7})_2MoO_2]$ (in methanol-d_4 or $CDCl_3$) does not show any characteristic signals. Only broad resonances can be observed which is due to the presence of a mixture of isomers (vide infra). However, the complexes can be characterized by means of mass spectrometry and elemental analysis. Typical peaks are observed in the positive

FAB-MS spectra in DMSO/3-NBA at $m/z = 885$ $[H_3(\mathbf{5})_2MoO_2]^+$, 805 $[HK_2(\mathbf{6})_2MoO_2]^+$ and 843 $[K_3(\mathbf{6})_2MoO_2]^+$, or at $m/z = 1187$ $[HK_2(\mathbf{7})_2MoO_2]^+$ and 1225 $[K_3(\mathbf{7})_2MoO_2]^+$. Observation of some peaks in the negative ESI-MS in methanol which can be attributed to methanol adducts (e.g., $m/z = 953$ $[K(\mathbf{5})_2MoO_2(MeOH)]^-$) give an indication that the tweezer-type complexes indeed are able to interact with small guest molecules (at least in the gas phase).

8-Hydroxyquinoline complexes of ligands **9** and **10** are obtained by reaction of three equivalents of **9-H** or **10-H** with one equivalent of gallium trisacetylacetonate. Volatile components are pumped off in vacuum and the tris-quinolinato complexes $[(\mathbf{9})_3Ga]$ and $[(\mathbf{10})_3Ga]$ remain. Again no characteristic NMR spectra are observed, but mass spectrometry and elemental analysis reveal the presence of the coordination compounds. In addition, IR spectroscopy shows the typical C–O stretching frequencies for coordinated quinolinates at 1110 cm^{-1} $[(\mathbf{9})_3Ga]$ and 1116 cm^{-1} $[(\mathbf{10})_3Ga]$.[25]

For the gallium complexes $[(\mathbf{9}/\mathbf{10})_3Ga]$ a meridional (C_1-symmetry) and a facial (C_3-symmetry) isomer can be formed (Figure 3).[26]

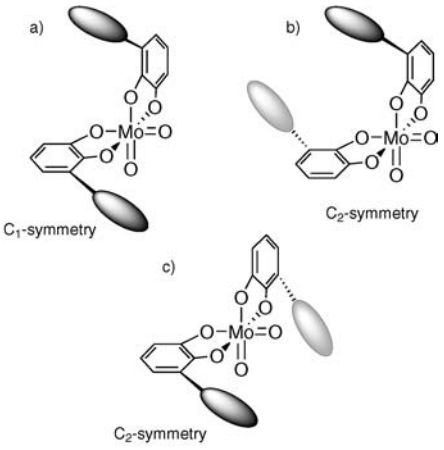


Figure 3 Schematic representation of the possible isomers of biscatecholate molybdenumdioxo complexes (only one of the two enantiomeric forms of the isomers is shown and the substituents are only indicated)

In case of the molybdenum(VI)dioxo derivatives, three different types of complexes can be formed (Figure 3, a–c). Two of them possess a tweezer-type arrangement while the third possesses a geometry which is not predisposed for the binding of guests. One of the two tweezer-type complexes possesses C_1-, the other C_2-symmetry so that it should be possible to distinguish between those by NMR.[19]

The observation of only broad signals by NMR for the complexes indicates that a mixture of all isomers is present. Due to the non-covalent nature of the metal coordination, all species (Figure 3, a–c) should be in a dynamic equilibrium with each other. However, adding tetrabutyl ammonium nitrate to a solution of $K_2[(\mathbf{5})_2MoO_2]$ in $CDCl_3$ reveals an NMR spectrum which becomes more and more simple and finally results in only one set of signals for the ligands (Figure 4).

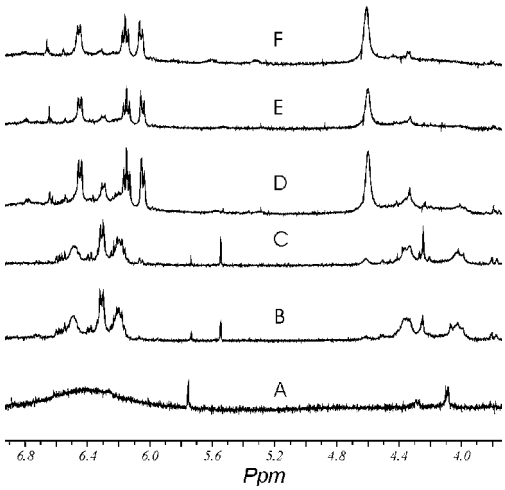


Figure 4 Part of the ^1H NMR spectra of $[(\mathbf{5})_2MoO_2]^{2-}$ at room temperature in $CDCl_3$ in the absence (A) and in the presence of nitrate (B: 10 min after addition of nitrate; C: 1 day after addition; D: 10 weeks after addition; E: 13 weeks after addition; F: 18 weeks after addition)

Characteristic resonances are observed for the catechol unit at $\delta = 6.45$ (d, $J = 7.9$ Hz), 6.16 (t, $J = 7.9$ Hz), 6.06 (d, $J = 7.9$ Hz) and for the methylene unit of the glycine at $\delta = 4.61$ (s) (Figure 4, F). This result indicates that the nitrate anions are able to bind to one of the isomers of complex $[(\mathbf{5})_2MoO_2]^{2-}$ and the allosteric effect between strong metal coordination and weak binding of the nitrate favors the formation of this one isomer. Some additional stabilization might be obtained by a hydrophobic interaction between the tetrabutyl ammonium cation with the apolar alkyl chains. The observation of only one set of ligand signals indicates that the C_2-symmetric complex shown in Figure 3b is the favored host for tetrabutylammonium nitrate.

In this paper we presented the synthesis of catechol and 8-hydroxyquinoline ligands which bear glycine-*N*-amide based side chains. Upon coordination of the catechol derivatives to molybdenum(VI)dioxo or the hydroxyquinolines to gallium(III), mixtures of isomeric coordination compounds are formed. Preliminary binding studies with anions show that the molybdenumdioxo bis(catecholate) complexes bind nitrate anions (also they are negatively charged). Allosteric behavior can be observed between metal and nitrate binding.

Also the association between receptor and substrate is very low in the examples which we presented in this study. We believe that we are on the way to develop new host/guest systems based on metal complex units. As one example, preliminary gas phase studies with the gallium complexes show that spherical ions (chloride, bromide, iodide)[27] can be bound by those complexes. Future work will focus on different – more complicated – side-chains which are able to bind not only anions but also small or-

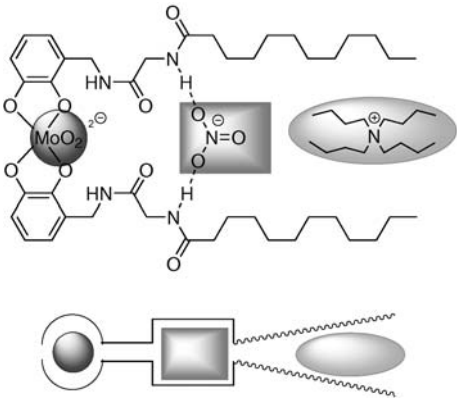


Figure 5

ganic molecules. A goal for the future of this program will be to get some communication (by means of stereochemistry, reactivity or electron transfer) established between the metals and a bound guest as it is observed e.g. in metalloenzymes.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 500 or AM 400 spectrometer using DEPT techniques for the assignment of the multiplicity of carbon atoms. FT-IR spectra were recorded by diffuse reflection (KBr) on a Bruker IFS spectrometer. Mass spectra (EI, 70 eV; FAB with DMSO/3-NBA as matrix) were taken on a Finnigan MAT 90 mass spectrometer. ESI-MS were detected using a Bruker Bioapex II FTMS equipped with a 7 Tesla magnet. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyzer. UV/Vis spectra were recorded on a Perkin Elmer Lambda 2 spectrometer. Melting points: Büchi B-540 (uncorrected). Solvents were purified by standard methods.

***N*-Dodecanoylglycine (2a)**

Glycine (284 mg, 3.78 mmol) is dissolved in aq NaOH (2 mL, 2 M). After simultaneous addition of laurinic acid chloride (1.76 mL, 7.41 mmol) in Et_2O (2 mL) and aq. NaOH (2 mL, 2 M) the resulting mixture is stirred for 1 h. The solution is acidified by addition of aq HCl (20%) and the precipitate is filtered off and washed with CH_2Cl_2.

Yield: 437 mg (45%) of a white solid.

Mp 125 °C.

IR (KBr): 3321, 3082, 2954, 2919, 2850, 1741, 1704, 1645, 1560, 1471, 1406, 1272, 1256, 1039, 869, 720, 688 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.09 (br s, 1 H), 3.68 (d, *J* = 5.8 Hz, 2 H), 2.07 (t, *J* = 7.5 Hz, 2 H), 1.45 (m, 2 H), 1.21 (m, 16 H), 0.83 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 173.0 (C), 171.9 (C), 35.5 (CH_2), 31.8 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 25.6 (CH_2), 22.6 (CH_2), 14.4 (CH_3).

MS (EI, 70 eV): *m*/*z* = 257 [M]$^+$, 117.

HRMS: *m*/*z* calcd for $C_{14}H_{27}NO_3$: 257.1991; found: 257.1995.

Anal. Calcd for $C_{14}H_{27}NO_3 \cdot H_2O$: C, 61.06; H, 10.61; N, 5.09. Found: C, 59.46; H, 9.36; N, 4.80.

***N*-Benzoylglycine (2b)**

Compound **2b** is prepared as described for **2a** starting form glycine (400 mg, 5.33 mmol) and benzoylchloride (614 μL, 5.33 mmol).

Yield: 386 mg (41%, 2.15 mmol), white solid.

Mp 181 °C.

IR (KBr): 3342, 3073, 2939, 2692, 2605, 2479, 1988, 1925, 1746, 1707, 1600, 1572, 1559, 1492, 1417, 1396, 1336, 1318, 1304, 1258, 1184, 1080, 1000, 851, 807, 725, 695, 661 cm^{-1}.

^{1}H NMR (CD_3OD): δ = 7.58–7.53 (m, 2 H), 7.52–7.44 (m, 3 H), 3.30 (s, 2 H).

^{13}C NMR (CD_3OD): δ = 171.7 (C), 169.1 (C), 133.7 (C), 131.5 (CH), 128.2 (CH, double intensity), 127.0 (CH, double intensity), 40.9 (CH_2).

MS (EI, 70 eV): *m*/*z* = 179 [M]$^+$, 105.

HRMS: *m*/*z* calcd for $C_9H_9NO_3$: 179.0582; found: 179.0579.

Anal. Calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.70; H, 5.24; N, 6.92.

***N*-Dodecanoylglycine(2,3-dimethoxybenzyl)amide (3a)**

Glycine derivative **2a** (1.29 g, 5.00 mmol) and Hünig's base (ethyl diisopropyl amine, 942 μL, 5.50 mml) are dissolved in CH_2Cl_2 (30 mL). First HBTU (2.28g, 6.00 mmol) in DMF (20 mL) and after 1 h 2,3-dimethoxybenzylamine (**1**, 740 μL, 5.00 mmol) is added. After stirring over night the organic phase is washed with sat. aq NH_4Cl (3 ×), sat. aq $NaHCO_3$ (3 ×) and sat. aq NaCl (3 ×), dried ($MgSO_4$) and the solvent is removed in vacuum.

Yield: 1.50 g (74%), white solid.

Mp 85 °C.

IR (KBr): 3303, 3077, 2921, 2850, 1634, 1589, 1549, 1484, 1276, 1219, 1085, 1005, 848, 748 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 6.97 (t, *J* = 7.9 Hz, 1 H), 6.93 (br s, 1 H), 6.82 (d, *J* = 7.9 Hz, 2 H), 6.62 (br s, 1 H), 4.42 (d, *J* = 6.0 Hz, 2 H), 3.89 (d, *J* = 5.2 Hz, 2 H), 3.83 (s, 6 H), 2.18 (t, *J* = 7.8 Hz, 2 H), 1.56 (m, 2 H), 1.26 (m, 16 H), 0.86 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 173.9 (C), 168.9 (C), 152.6 (C), 147.0 (C), 131.4 (C), 124.2 (CH), 121.1 (CH), 111.9 (CH), 60.7 (CH_3), 55.7 (CH_3), 43.2 (CH_2), 38.7 (CH_2), 36.3 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2, double intensity), 29.3 (CH_2), 25.6 (CH_2), 22.7 (CH_2), 14.1 (CH_3).

pos FAB-MS (DMSO/3-NBA): *m*/*z* = 407 [M + H]$^+$, 429 [M + Na]$^+$.

HRMS: *m*/*z* calcd for $C_{23}H_{39}N_2O_4$: 407.2910; found: 407.2901.

Anal. Calcd for $C_{23}H_{38}N_2O_4 \cdot H_2O$: C, 65.06; H, 9.50; N, 6.60. Found: C, 65.76; H, 9.39; N, 7.12.

***N*-Benzoylglycine(2,3-dimethoxybenzyl)amide (3b)**

3b is prepared from **2b** (200 mg, 1.12 mmol) as described for the preparation of **3a**.

Yield: 303 mg (82%), slightly yellow solid.

Mp 142 °C.

IR (KBr): 3288, 3071, 2997, 2933, 2833, 1955, 1909, 1772, 1669, 1645, 1603, 1580, 1558, 1484, 1431, 1400, 1375, 1362, 1344, 1328, 1279, 1241, 1223, 1173, 1101, 1078, 1048, 1028, 1002, 776, 749, 715, 690, 639 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.77 (dd, *J* = 7.8, 1.4 Hz, 2 H), 7.49–7.46 (m, 1 H), 7.40–7.37 (m, 2 H), 7.35 (t, *J* = 4.8 Hz, 1 H), 7.02 (t, *J* = 5.9 Hz, 1 H), 6.98 (t, *J* = 7.8 Hz, 1 H), 6.87 (dd, *J* = 7.8, 1.4 Hz, 1 H), 6.83 (dd, *J* = 8.2, 1.4 Hz, 1 H), 4.47 (d, *J* = 5.9 Hz, 2 H), 4.12 (d, *J* = 4.8 Hz, 2 H), 3.83 (s, 6 H).

^{13}C NMR ($CDCl_3$): δ = 168.8 (C), 167.7 (C), 152.6 (C), 147.1 (C), 133.5 (C), 131.8 (C), 131.4 (CH), 128.5 (CH, double intensity), 127.1 (CH, double intensity), 124.2 (CH), 121.2 (CH), 122.0 (CH), 60.7 (CH_3), 55.7 (CH_3), 43.7 (CH_2), 38.9 (CH_2).

MS (EI, 70 eV): *m*/*z* = 328 [M]$^+$, 166.

HRMS: *m*/*z* calcd for $C_{18}H_{20}N_2O_4$: 328.1423; found: 328.1428.

Anal. Calcd for $C_{18}H_{20}N_2O_4 \cdot 3/2H_2O$: C, 60.83; H, 6.52; N, 7.88. Found: C, 60.79; H, 6.00; N, 7.63.

***N*-*t*-Butoxycarbonylglycine(2,3-dimethoxybenzyl)amide (3c)**
Compound **3c** is prepared from **2c** (200 mg, 1.12 mmol) as described for the preparation of **3a**. The crude product is purified by chromatographic work up (silica gel, hexane–EtOAc, 1:1).

Yield: 1.42 g (88%), yellow oil.

IR (KBr): 3571, 3278, 3078, 2978, 2937, 2835, 1700, 1666, 1522, 1482, 1274, 1171, 1091, 1060, 1004, 788, 750 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 6.99 (t, *J* = 7.9 Hz, 1 H), 6.85 (m, 2 H), 6.57 (br s, 1 H), 5.29 (br s, 1 H), 4.46 (d, *J* = 5.9 Hz, 2 H), 3.85 (s, 3 H), 3.84 (s, 3 H), 3.77 (d, *J* = 4.7 Hz, 2 H), 1.41 (s, 9 H).

^{13}C NMR ($CDCl_3$): δ = 169.1 (C), 156.0 (C), 152.6 (C), 147.1 (C), 131.5 (C), 124.2 (CH), 121.2 (CH), 112.0 (CH), 80.1 (C), 60.7 (CH_3), 55.7 (CH_3), 44.3 (CH_2), 38.8 (CH_2), 28.3 (CH_3).

MS (EI, 70 eV): *m*/*z* = 324 $[M]^+$, 166.

HRMS: *m*/*z* calcd for $C_{16}H_{24}N_2O_5$: 324.1685, found: 324.1692.

Anal. Calcd for $C_{16}H_{24}N_2O_5 \cdot 1/2H_2O$: C, 57.64; H, 7.56; N, 8.40. Found: C, 57.29; H, 7.31; N, 8.73.

***N*-(*n*-Octadecylaminocarbonyl)glycine(2,3-dimethoxybenzyl)amide (4) via Glycine(2,3-dimethoxybenzyl)amide Hydrochloride**
The BOC-protected derivative **3c** is stirred for 3 h in a sat. soln of HCl in Et_2O at r.t. The precipitated glycine(2,3-dimethoxybenzyl)amide hydrochloride is used without further purification.

Under argon glycine(2,3-dimethoxybenzyl)amide hydrochloride (200 mg, 0.76 mmol) is dissolved in CH_3CN (40 mL) and *N*-methylmorpholine (NMM, 84 μL, 0.76 mmol) is added. After 20 min at r.t. *n*-octadecylisocyanate (224 mg, 0.76 mmol) is added and the mixture is stirred over night. The product precipitates and is isolated by filtration.

Yield: 329 mg (83%), white solid.

Mp: 145 °C.

IR (KBr): 3381, 3306, 3081, 2923, 2848, 2596, 2265, 1651, 1609, 1555, 1509, 1486, 1467, 1444, 1392, 1277, 1231, 1219, 1085, 1002, 779, 750 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.01 (t, *J* = 8.0 Hz, 1 H), 6.81 (d, *J* = 8.0 Hz, 2 H), 6.53 (br t, 1 H), 4.89 (br t, 1 H), 4.46 (d, *J* = 5.9 Hz, 2 H), 4.42 (br t, 1 H), 3.86 (d, overlaid, 2 H), 3.86 (s, 6 H), 3.15 (q, *J* = 6.5 Hz, 2 H), 1.47 (m, 2 H), 1.25 (m, 30 H), 0.87 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 169.8 (C), 157.9 (C), 152.6 (C), 147.2 (C), 131.4 (C), 124.2 (CH), 121.3 (CH), 112.0 (CH), 60.7 (CH_3), 55.8 (CH_3), 44.3 (CH_2), 40.8 (CH_2), 38.9 (CH_2), 31.9 (CH_2), 30.1 (CH_2), 29.7 (CH_2, six fold intensity), 29.7 (CH_2, double intensity), 29.6 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 26.9 (CH_2), 22.7 (CH_2), 14.1 (CH_3).

FAB-MS (Pos., DMSO/3-NBA): *m*/*z* = 520 $[M + H]^+$.

HRMS: *m*/*z* calcd for $C_{30}H_{54}N_3O_4$: 520.4114; found: 520.4120.

Anal. Calcd for $C_{30}H_{53}N_3O_4$: C, 69.32; H, 10.28; N, 8.08. Found: C, 69.13; H, 10.00; N, 8.17.

Cleavage of Methyl Aryl Ethers; General Procedure
The dimethoxybenzene derivative (approx. 1 mmol) is dissolved in CH_2Cl_2 anhyd (15 mL) under argon and BBr_3 (2.5 equiv) is added. After 3 h the mixture is cooled in an ice bath and CH_3OH (10 mL) is added. The solvent is removed and the crude product is dissolved in CH_3OH which is removed again. Water is added to the residue and the mixture is treated with ultrasound. The product precipitates, is collected by filtration and dried in vacuum.

***N*-Dodecanoylglycine(2,3-dihydroxybenzyl)amide (5-H_2)**
Yield: 80%, white solid.

Mp 126 °C

IR (KBr): ν (cm^{-1}) = 3411, 3344, 3299, 3090, 2921, 2851, 1751, 1676, 1669, 1646, 1596, 1560, 1540, 1481, 1286, 1265, 734.

^1H NMR ($CDCl_3$): δ = 8.68 (br s, 1 H), 8.47 (br s, 1 H), 8.12 (m, 3 H), 6.62 (br s, 1 H), 6.56 (br s, 1 H), 4.26 (br s, 2 H), 4.00 (br s, 2 H), 2.38 (br s, 2 H), 1.56 (br s, 2 H), 1.27 (m, 16 H), 0.86 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 178.3 (C), 170.5 (C), 145.3 (C), 142.6 (C), 123.9 (C), 121.9 (CH), 120.6 (CH), 115.6 (CH), 31.9 (CH_2, double intensity), 29.6 (CH_2, double intensity), 29.5 (CH_2), 29.4 (CH_2, double intensity), 29.3 (CH_2), 29.2 (CH_2), 25.7 (CH_2), 22.7 (CH_2, double intensity), 14.1 (CH_3).

FAB-MS (Pos., DMSO/3-NBA): *m*/*z* = 379 $[M + H]^+$, 401 $[M + Na]^+$.

Anal. Calcd for $C_{21}H_{34}N_2O_4 \cdot 2/3H_2O$: C, 64.59; H, 9.12; N, 7.17. Found: C, 64.14; H, 8.77; N, 6.84.

***N*-Benzoylglycine(2,3-dihydroxybenzyl)amide (6-H_2)**
Yield: 65%, beige solid.

Mp 152 °C (decomp.).

IR (KBr): 3500, 3435, 3299, 3089, 1898, 1767, 1642, 1538, 1284, 740, 709 cm^{-1}.

^1H NMR (CD_3OD): δ = 7.88–7.86 (m, 2 H), 7.55–7.52 (m, 1 H), 7.47–7.44 (m, 2 H), 6.71–6.68 (m, 2 H), 6.64–6.61 (m, 1 H), 4.37 (s, 2 H), 4.06 (s, 2 H).

^{13}C NMR (CD_3OD): δ = 170.9 (C), 169.1 (C), 145.2 (C), 143.1 (C), 133.6 (C), 131.5 (CH), 128.2 (CH, double intensity), 127.1 (CH, double intensity), 124.8 (C), 119.9 (CH), 119.2 (CH), 114.2 (CH), 42.5 (CH_2), 38.6 (CH_2).

MS (EI, 70 eV): *m*/*z* = 300 $[M]^+$, 105.

HRMS: *m*/*z* calcd for $C_{16}H_{16}N_2O_4$: 300.1110; found: 300.1117.

Anal. Calcd for $C_{16}H_{16}N_2O_4 \cdot H_2O$: C, 60.37; H, 5.70; N, 8.80. Found: C, 60.65; H, 5.39; N, 8.51.

***N*-(*n*-Octadecylaminocarbonyl)glycine(2,3-dihydroxybenzyl)amide (7-H_2)**
Yield: 79%, white solid.

Mp 135 °C.

IR (KBr): 3409, 3326, 2849, 1649, 1619, 1578, 1544, 1481, 1464, 1376, 1342, 1292 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 8.19 (br s, 1 H), 6.64 (t, *J* = 4.5 Hz, 1 H), 6.54 (m, 2 H), 6.10 (br s, 1 H), 6.02 (br s, 1 H), 4.17 (s, 2 H), 3.64 (d, *J* = 5.2 Hz, 2 H), 2.94 (m, 2 H), 1.32 (m, 2 H), 1.21 (m, 30 H), 0.83 (t, *J* = 6.5 Hz, 3 H).

^{13}C NMR (DMSO-d_6): δ = 171.2 (C), 158.4 (C), 145.6 (C), 143.4 (C), 126.3 (C), 119.5 (CH), 119.1 (CH), 114.7 (CH), 43.3 (CH_2), 38.1 (CH_2), 31.7 (CH_2, double intensity), 30.4 (CH_2), 29.5 (CH_2, six fold intensity), 29.3 (CH_2), 29.2 (CH_2, double intensity), 28.8 (CH_2), 26.9 (CH_2), 22.5 (CH_2, double intensity), 19.2 (CH_2), 14.4 (CH_3).

FAB-MS (Pos., DMSO/3-NBA): *m*/*z* = 492 $[M + H]^+$, 514 $[M + Na]^+$.

HRMS: *m*/*z* calcd for $C_{28}H_{50}N_3O_4$: 492.3801; found: 492.3790.

Anal. Calcd for $C_{28}H_{49}N_3O_4 \cdot 0.25H_2O$: C, 67.77; H, 10.05; N, 8.47. Found: C, 67.40; H, 9.54; N, 8.66.

***N*-Dodecanoylglycine(8-hydroxy-7-quinolinyl)amide (9-H)**
Hünig's base (116 μL, 0.68 mmol) and **2a** (160 mg, 0.62 mmol) are dissolved in CH_2Cl_2 (5 mL) and HBTU (281 mg, 0.74 mmol) in DMF (2 mL) is added. After 30 min at r.t., 7-amino-8-hydroxyquinoline (**8a**, 100 mg, 0.62 mmol) is added and the mixture is stirred over night. The precipitate is filtered off and dried in vacuum.

Yield: 84 mg (34%), white solid.

Mp 145 °C.

IR (KBr): 3324, 2949, 2921, 1675, 1638, 1548, 1532, 1506,1432, 1371, 1328, 1293, 1275, 1243, 1208, 1187, 829, 663 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 9.38 (s, 1 H), 8.82 (d, *J* = 3.5 Hz, 1 H), 8.28 (m, 2 H), 8.21 (d, *J* = 8.9 Hz, 1 H), 7.46 (dd, *J* = 8.3, 3.5 Hz, 1 H), 7.37 (d, *J* = 8.9 Hz, 1 H), 3.95 (d, *J* = 5.7 Hz, 2 H), 2.15 (t, *J* = 7.4 Hz, 2 H), 1.51 (t, *J* = 6.5 Hz, 2 H), 1.20 (m, 16 H), 0.82 (t, *J* = 6.5 Hz, 3 H).

^{13}C NMR (DMSO-d_6): δ = 173.4 (C), 168.7 (C), 149.0 (CH), 142.5 (C), 138.7 (C), 136.4 (CH), 125.7 (C), 123.7 (C), 122.5 (CH), 121.1 (CH), 117.4 (CH), 43.4 (CH_2), 35.7 (CH_2), 31.7 (CH_2), 29.5 (CH_2, double intensity), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 25.7 (CH_2), 22.5 (CH_2), 14.4 (CH_3).

MS (EI, 70 eV): *m*/*z* = 399 $[M]^+$, 187.

HRMS: *m*/*z* calcd for $C_{23}H_{33}N_3O_3$: 399.2522; found: 399.2520

Anal. Calcd for $C_{23}H_{33}N_3O_3 \cdot 0.25H_2O$: C, 69.14; H, 8.33; N, 10.52. Found: C, 68.37; H, 8.36; N, 10.40.

***N*-Dodecanoylglycine(8-hydroxy-7-quinolinylmethyl)amide (10-H)**
10-H is prepared similar to **9-H** using 7-aminomethyl-8-hydroxyquinoline (**8b**, 52 mg, 0.30 mmol). The crude product is recrystallized from $CHCl_3$.

Yield: 86 mg (70%), white solid.

Mp 189 °C.

IR (KBr): 3291, 2955, 2921, 2851, 1659, 1634, 1549, 1512, 1469, 1407, 1380, 1285, 1243, 845, 830 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 9.94 (s, 1 H), 8.85 (m, 1 H), 8.29 (m, 2 H), 8.07 (t, *J* = 5.8 Hz, 1 H), 7.53 (dd, *J* = 8.3, 4.1 Hz, 1 H), 7.39 (m, 2 H), 4.46 (d, *J* = 5.8 Hz, 2 H), 3.73 (d, *J* = 5.8 Hz, 2 H), 2.13 (t, *J* = 7.5 Hz, 2 H), 1.48 (m, 2 H), 1.22 (m, 16 H), 0.83 (t, *J* = 6.5 Hz, 3 H).

^{13}C NMR (DMSO-d_6): δ = 172.6 (C), 169.4 (C), 149.9 (C), 148.2 (CH), 137.9 (C), 136.0 (CH), 127.5 (C), 127.3 (CH), 121.5 (CH), 121.3 (C), 117.0 (CH), 42.1 (CH_2), 37.0 (CH_2), 35.2 (CH_2), 31.3 (CH_2), 29.0 (CH_2, double intensity), 28.9 (CH_2), 28.8 (CH_2), 28.7 (CH_2, double intensity), 25.1 (CH_2), 14.0 (CH_3).

MS (EI, 70 eV): *m*/*z* = 413 $[M]^+$, 173.

HRMS: *m*/*z* calcd for $C_{24}H_{35}N_3O_3$: 413.2678; found: 413.2689.

Anal. Calcd for $C_{24}H_{35}N_3O_3 \cdot 2H_2O$: C, 64.12; H, 8.74; N, 9.35. Found: C, 64.31; H, 8.30; N, 9.66.

Dicatechol-*cis*-dioxomolybdenum(VI) Complexes; General Procedure
Catechol ligand (2 equiv), $MoO_2(acac)_2$ (1 equiv) and Na_2CO_3 (1 equiv) in MeOH are stirred under argon. The solvent is removed and the residue is purified by filtration over Sephadex LH20. NMR spectroscopy shows only broad signals for the complexes.

$K_2[(5)_2MoO_2]$
Yield: 82%, red solid.

IR (KBr): 3399, 3056, 2923, 2853, 1634, 1527, 1463, 1329, 1281, 1252, 1216, 1116, 1071, 1028, 975, 889, 853, 739, 631 cm^{-1}.

ESI-MS (Neg., MeOH): *m*/*z* = 953 $\{[K(\mathbf{5})_2MoO_2]CH_3OH\}^-$.

FAB-MS (Pos., DMSO/3-NBA): *m*/*z* = 885 $[H_3(\mathbf{5})_2MoO_2]^+$.

UV/Vis (MeOH): λ_{max} = 202, 278 nm.

Anal. Calcd for $K_2[(C_{21}H_{32}N_2O_4)_2MoO_2] \cdot H_2O$: C, 51.63; H, 6.81; N, 5.73. Found: C, 51.49; H, 6.80; N, 5.47.

$K_2[(6)_2MoO_2]$
Yield: 44%, red solid.

IR (KBr): 3333, 3058, 2929, 1650, 1602, 1531, 1488, 1455, 1279, 1252, 889, 853, 738, 713, 632 cm^{-1}.

pos FAB-MS (DMSO/3-NBA): *m*/*z* = 843 $[K_3(\mathbf{6})_2MoO_2]^+$, 805 $[HK_2(\mathbf{6})_2MoO_2]^+$.

UV/Vis (MeOH): λ_{max} = 196, 275 nm.

Anal. Calcd for $K_2[(C_{16}H_{14}N_2O_4)_2MoO_2] \cdot 3H_2O$: C, 44.86; H, 4.00; N, 6.54. Found: C, 44.52; H, 4.56; N, 6.22.

$K_2[(7)_2MoO_2]$
Yield: 55%, red solid.

IR (KBr): 3332, 2919, 2851, 1652, 1568, 1457, 1330, 1276, 1071, 1029, 976, 889, 855, 738, 632 cm^{-1}.

neg. ESI-MS (MeOH): *m*/*z* = 1142 $\{[H(\mathbf{7})_2MoO_2]CH_3OH\}^-$, 1110 $\{[H(\mathbf{9})_2MoO_2]\}^-$.

pos. FAB-MS (DMSO/3-NBA): *m*/*z* = 1225 $[K_3(\mathbf{7})_2MoO_2]^+$, 1187 $[HK_2(\mathbf{7})_2MoO_2]^+$.

UV/Vis (MeOH): λ_{max} = 201, 278 nm.

Anal. Calcd for $K_2[(C_{28}H_{47}N_3O_4)_2MoO_2] \cdot 4H_2O$: C, 53.48; H, 8.18; N, 6.68. Found: C, 53.32; H, 7.80; N, 6.52.

Tris(hydroxyquinolinato)gallium(III) Complexes; General Procedure
8-Hydroxyquinoline ligand (3 equiv) is dissolved in MeOH and $Ga(acac)_3$ (1 equiv) is added. After 1 h at r.t. the solvent and 2,4-pentadione are removed in vacuum to obtain the complexes in quantitative yield. NMR spectroscopy shows only broad signals for the complexes.

$[(9)_3Ga]$
Yellow solid.

IR (KBr): 3304, 2925, 2854, 1663, 1608, 1589, 1522, 1502, 1456, 1427, 1377, 1323, 1294, 1205, 1110 cm^{-1}.

FAB-MS (Neg., DMSO/3-NBA): *m*/*z* = 1263 $[M - H]^-$.

ESI-MS (Neg., MeOH): *m*/*z* = 1299 $[M + Cl]^-$.

UV/Vis (MeOH): λ_{max} = 195, 216, 273, 326, 339, 402 nm.

Anal. Calcd for $(C_{23}H_{32}N_3O_3)_3Ga \cdot H_2O$: C, 64.58; H, 7.70; N, 9.82. Found: C, 64.22; H, 7.46; N, 9.52.

$[(10)_3Ga]$
Yellow solid.

IR (KBr): 3303, 2924, 2853, 1653, 1533, 1504, 1457, 1377, 1192, 1116, 846, 754 cm^{-1}.

FAB-MS (Neg., DMSO / 3-NBA): m/z = 1307 $[M-H]^-$.

ESI-MS (Neg., MeOH): *m*/*z* = 1341 $[M + Cl]^-$.

UV/Vis (MeOH): λ_{max} = 195, 260, 382 nm.

Anal. Calcd for $(C_{24}H_{34}N_3O_3)_3Ga{\cdot}5H_2O$: C, 61.88; H, 8.08; N, 9.02. Found: C, 61.85; H, 8.07; N, 8.65.

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