Chiral S-1,1'-bi-2-naphthol (S-BINOL) as a synthon for supramolecular hydrogen-bonded \{(S-BINOL)\}(S-BINOL) strands with naphthyl-paneled cavities or channels for a Cd(NH₃)₄ fragment \(n = 2\) or \[Ag(NH₃)₂\] \(n = 1\). Part 2†

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Received 14th February 2005, Accepted 19th April 2005

First published as an Advance Article on the web 26th April 2005

The molecule 1,1'-bi-2-naphthol (BINOL) shows a propensity for supramolecular, hydrogen-bonded strand formation when crystallized with its deprotonated form BINOLAT²⁻ or BINOLAT⁻ (in conc. ammonia). The strand adapts from racemic rac-BINOL to enantiomeric S-BINOL and from di- to monocatonic metal ions but keeps the overall strand feature. The structure of [Cd²⁺(S-BINOL)²-x²O₂S⁻(NH₃)₆][S-BINOL]₂(H₂O)(MeOH) (I) can be correlated to the known structures of [M(NH₃)₆]²⁺(rac-BINOLAT)²⁻(rac-BINOL)₂ (M = Ni, Cd) despite the direct Cd-O, O'-BINOLAT chelate coordination in the former. With Ag⁺ as a mononuclear metal structures of the formula [Ag(NH₃)₂]⁻(S-BINOL)²⁻(S-BINOL)(EtOH) (2) and [Ag(NH₃)₄]⁺(S-BINOL)²⁻(S-BINOL)(H₂O)(MeOH) (3) are formed from ethanol or methanol, respectively.

Crystallization of Ag⁺NH₃ with rac-BINOL from EtOH also yields 2 with a spontaneous resolution to an enantiomeric excess of ca. 40%. Simultaneous differential thermoanalysis, thermogravimetry and mass spectrometry (DTA-TG-MS) show that the EtOH, MeOH and H₂O solvent of crystallization together with the NH₃ ligands can be removed before the BINOL moieties. X-Ray powder diffraction (XRPD) still shows the sample of 1 to be crystalline after the loss of solvent of crystallization. Upon heating to 130 °C the needle-shaped crystals of 2 keep their shape, yet darken (formation of Ag by XRPD) and turn amorphous, with small crystal “prickles” (BINOL by XRPD) forming on the surface. The difference in metal coordination between 1 and [Cd(NH₃)₆]²⁺(rac-BINOLAT)²⁻(rac-BINOL)₂ is evidenced by a strong maximum at 591 nm in the emission spectrum of I which is absent in the emission spectra of both BINOL and [Cd(NH₃)₆]²⁺(rac-BINOLAT)²⁻(rac-BINOL)₂. This maximum is assigned to a metal–ligand transition due to the direct Cd-O, O'-BINOLAT chelate coordination in I.

Introduction

The field of crystal engineering deals with the predictable assembly of supramolecular systems such as organic molecular solids and metal coordination compounds (coordination polymers).₁–₅ Recent work indicates an interest in the use of enantiomeric or racemic 1,1'-bi-2-naphthol/acetone (BINOL/acetone) for the construction of (chiral) superstructures with Co₂(C₆H₃O)₂Cl₂,₆ with alkali cations,⁷ with volatile guests (1,4-dioxane, morpholine, dimethylsulfoxide, acetone and tetrahydrofuran),₈ with prochiral guests (α,β-unsaturated compounds, piperazinedione derivatives),₉ with 2,2'-bipyridine and naphthodiazine,₁₀ or with benzoquinone and aromatic hydrocarbons showing a molecular recognition ability towards the latter.₁₁ Furthermore, from the functionalization of BINOL and the related ligand 2,2'-diamino-1,1'-(naphthyl) building blocks are derived for the construction of chiral ligands for coordination and metallosupramolecular chemistry. The BINOL unit is readily functionalized with ligating groups at both the diol oxygen atoms and at a variety of positions on the binaphthyl rings.₁₂ Also, condensation of aromatic aldehydes with 2,2'-diamino-1,1'-binaphthyl or 2-amino-2'-hydroxy-1,1'-binaphthyl affords various chiral binaphthyl Schiff-base ligands which as their chiral metal complexes are active catalysts for a number of stereoselective organic transformations.₁₃ Metal complexes allow for the pre-orientation of the building blocks according to the metal coordination geometry.₁₄ One strategy for the construction of supramolecular architectures is by second-sphere coordination—the interaction between already coordinatively saturated metal complexes and external ligands, e.g. through hydrogen bonding.₁₅,₁₆ To enable supramolecular second-coordination sphere systems, functional groups must be appended to the first-sphere ligand, thereby not coordinating to a metal center but to bind the external second-sphere ligands. We have already reported on the second-sphere coordination of metal complexes with the ligands 5,5'-bis(ethoxy carbonylamino)-2,2'-bipyridine or 5,5'-diamino-2,2'-bipyridine to anions and crown ethers through N-H···X hydrogen bonding from the amide or amino groups, respectively.
Subsequently, we have investigated the supramolecular organization of rac-BINOL and its dianion (BINOLAT$^{2-}$) as chiral building blocks. The naphthyl-paneled cavities in the \((\text{rac-BINOLAT}^2)_(\text{BINOL}_2)\)-``host'' strands in the structures of \([\text{M(NH}_3]_n]^{1+}(\text{rac-BINOLAT}^2)\)\((\text{rac-BINOL})_2\) accommodate the \([\text{M(NH}_3]_n]^{1+}``guest'' cation through second-sphere N–H…O hydrogen bonding irrespective of the size (M ~ Ni or Cd, n ~ 6) or coordination polyhedron (tetrahedron for M ~ Zn, n ~ 4 or octahedron for M ~ Ni, Cd) (Scheme 1).

Here we extend our investigations on BINOL as a supramolecular synthon with the use of enantiomeric S-BINOL with dicationic Cd$^{2+}$ and with monocationic Ag$^+$ as a metal.

### Results and discussion

**Crystal structure of \([\text{Cd}^{2+}(\text{S-BINOLAT}^2)\cdot\text{O}_2\cdot\text{O}'](\text{NH}_3)_4\cdot(\text{S-BINOL})_2(\text{H}_2\text{O})(\text{MeOH})_2\) (1)** in correlation to \([\text{Cd}(\text{NH}_3)_6]^{2+}(\text{rac-BINOLAT}^2)\text{((rac-BINOL)}_2\)

Starting from S-BINOL, we could obtain crystals with cadmium as a metal under otherwise identical conditions than for the rac-BINOL [eqns. (1) and (2)]. The changes in the product are quite profound: A different formula composition and coordination environment for Cd (see below) and a different crystal form (Fig. 1).

\[
\text{Cd}^{2+} + 3 \text{rac-BINOL} \xrightarrow{\text{conc. NH}_3, \text{MeOH}} [\text{Cd}^{2+}(\text{NH}_3)_6]\text{(rac-BINOLAT}^2\text{)}\text{(rac-BINOL)}_2 \quad (1)
\]

\[
\text{Cd}^{2+} + 3 \text{S-BINOL} \xrightarrow{\text{conc. NH}_3, \text{MeOH}} [\text{Cd}^{2+}(\text{S-BINOLAT}^2\text{)}\text{(S-BINOL)}_2(\text{H}_2\text{O})(\text{MeOH})_2] \quad (2)
\]

We can derive and understand the structure of 1 through a development from the known structure of \([\text{Cd}(\text{NH}_3)_6]^{2+}(\text{rac-BINOLAT}^2\text{)}\text{(rac-BINOL)}_2\) (see Scheme 1). Scheme 2 illustrates the alternation of the R- and S-configured BINOL (and BINOLAT) along the strand in \([\text{Cd}(\text{NH}_3)_6]^{2+}(\text{rac-BINOLAT}^2\text{)}\text{(rac-BINOL)}_2\).
Using enantiomeric S-BINOL, the R-configured units “have to be replaced” by the S-forms as is formally done in Scheme 3. As a consequence, the hydrogen bonding between the “new” peripheral S-BINOL and the central S-BINOLAT no longer matches and these “newly introduced” S-BINOL molecules “move” away from the central BINOLAT. The gap is filled and bridged by the water and methanol molecules through hydrogen bonding (not shown here).

Still the cavities from the racemic structure (Scheme 1) are preserved in the \(((S\text{-BINOLAT}^2\text{)}(S\text{-BINOL})_2)\)-strand and are again filled with the Cd-cations as a Cd(NH$_3$)$_6$-fragment (Scheme 4). Perhaps as a result of the change in hydrogen bonding between BINOL and BINOLAT the metal atom now coordinates to the two oxygen atoms of the BINOLAT$^{2-}$ (Fig. 2). The Cd atom sits on the two-fold axis which bisects the X–Cd–X' angles (X = O$_3$, N$_1$, N$_2$).

In the series of Figs. 3–6 the strand and cavity formation in 1 together with the hydrogen bonding interactions are illustrated. The ammine ligands of the Cd(NH$_3$)$_4$ fragments are also connected with the BINOLAT/BINOL units through N–H…O hydrogen bonding (Fig. 4, Table 1). The hydrogen bonding between the BINOLAT/BINOL units together with the H$_2$O and MeOH solvent molecules lead to the actual strand formation along c.

The space filling representation of the strand structure of 1 (Fig. 5) shows that all cavities are opened to the same side of the strand which is different from the strand structure in the racemic [Cd(NH$_3$)$_6$]$^{2+}$/(rac-BINOLAT)$^2-$ (Fig. 2). The voids opened alternately to opposite sides.

The outside of the strands is hydrophobic/lipophilic and neighboring strands are hexagonally closed-packed along a and b (Fig. 6).

Crystal structures of [Ag$^+$(NH$_3$)$_2$](S-BINOLAT$^-$)(S-BINOL)(EtOH) (2) and [Ag$^+$(NH$_3$)$_2$](S-BINOLAT$^-$)(S-BINOL)(H$_2$O)$_2$(MeOH) (3)

Crystals of [Ag$^+$(NH$_3$)$_2$](S-BINOLAT$^-$)(S-BINOL)(EtOH) (2) could be grown from the reaction of a 1 : 1 molar ratio of AgNO$_3$ with S-BINOL in a mixture of ammonia(26%)/ethanol [eqn. (3)]. The same compound also crystallized if rac-BINOL was used instead of the enantiomeric S-form through spontaneous resolution to an enantiomeric excess of ca. 40% in the investigated single crystal (according to the
The reaction and crystal growth from 1:1 AgNO$_3$ with S-BINOL could also be carried out in a mixture of ammonia(26%)/methanol which necessarily led to a change in solvent molecules of crystallization and gave [Ag$^+$ (NH$_3$)$_2$](S-BINOL$^-$)(S-BINOL)(H$_2$O)$_2$(MeOH) (3) [eqn. (5)].

We were studying the supramolecular arrangement with a monocation, such as Ag$^+$ in the form of its diammine complex, in view of the noted similarity in the {S-BINOL$^-$}(S-BINOL)$_2$-"host" strands in the structures of [M(NH$_3$)$_6$]$_2$"(rac-BINOL)$^-$"(rac-BINOL)$_2$ which was the same regardless of the size (M = Ni or Cd, n = 6) or coordination polyhedron (tetrahedron for M = Zn, n = 4 or octahedron for M = Ni, Cd) (cf. Scheme 1). In the silver compounds 2 and 3 again a strand-like hydrogen-bonded BINOL/BINOL substructure forms, albeit different from those of dications. In 2 and 3 the (S-BINOL$^-$)(S-BINOL)-strand forms U-shaped channels on both sides of the strand. These channels or grooves are then filled by the diammine–silver complexes. Both structures of 2 and 3 are highly similar with respect to the formation of the strand, its shape and the incorporation of the [Ag(NH$_3$)$_2$]$^+$ cations, which is schematically depicted in Scheme 5.

The naphthoxide oxygen atom of the singly deprotonated S-BINOL is an acceptor of two hydrogen bonds, one from an OH group of another S-BINOL and the other from an OH group of the S-BINOL. This hydrogen-bonding mode gives rise to a BINOL/BINOL strand formation along a (Fig. 7). The ethanol molecules are connected with the BINOL/BINOL strand through hydrogen-bonding between the oxygen atom of ethanol and an OH group of S-BINOL. The strands extend collinearly along the crystallographic a-axis. The naphthyl panels flank the channel walls. The U-shaped channels may be better appreciated from a space-filling drawing in Fig. 8 which also shows the incorporation of the diammine–silver complexes. The linear ammine–silver environment in the first-sphere complex [Ag(NH$_3$)$_2$]$^+$ is typical (see legend to Fig. 8 for distances and angles). The [Ag(NH$_3$)$_2$]$^+$ fragments are connected with the BINOL/BINOL strand through N–H…O hydrogen bonding (Table 2). BINOL and the cation are in the center and surrounded by the BINOL molecules on the periphery of the strands. Silver–π interactions do not seem to play a role here because...
the silver–carbon distances are all greater than 3.0 Å, well beyond the limits from 2.40 to 2.77 Å observed in reported silver(I)–aromatic complexes.25,26 Along the adjacent strands interdigitate with their naphthyl groups so as to put a lid on the U-shaped channels of the neighboring strand (Fig. 9).

In the structure of 3 the BINOLAT/BINOL–hydrogen bonding is identical to the structure 2 yielding the same \{S-BINOLAT\}_2\cdot{S-BINOL}_2\}_{-\text{strand}} along b (Fig. 10, Table 3). The ethanol solvent of crystallization from structure 2 is replaced by a methanol and two water molecules in compound 3. These molecules are responsible for some weak inter-connectivity of adjacent BINOLAT/BINOL strands (see Table 3). Also, the difference in the molecules of solvation allows for the higher symmetric orthorhombic space group $P2_12_12_1$ in 3 versus triclinic $P1$ in 2. Other than that, the formation of U-shaped channels, the incorporation of the [Ag(NH$_3$)$_2$]$^+$ cations and the interdigitation of adjacent strands in 3 is as seen before in the structure of compound 2 (see Fig. 8 and 9).

### Table 1  Hydrogen bonding interactions in 1$^a$

<table>
<thead>
<tr>
<th>D–H–A</th>
<th>D–H/A</th>
<th>H–A/A_Å</th>
<th>D–A/A_Å</th>
<th>D–H–A_˚</th>
</tr>
</thead>
</table>
| \text{Intra-strand BINOL}→…\text{BINOLAT}:
O1–H1A→…O3$^3$ | 0.96(3) | 1.57(3) | 2.515(2) | 167(2) |
| Cd–NH3→…MeOH: | 0.90 | 2.20 | 3.065(4) | 161 |
| N2–H2C→…O1$^2$ | 0.90 | 2.38 | 2.869(3) | 114 |
| MeOH→…BINOL: | 1.01(3) | 1.74(3) | 2.698(3) | 157(3) |
| O4–H4A→…O3 | 1.74(3) | 2.773(3) | 157(3) |
| MeOH→…H2O: | 0.85(2) | 1.93(3) | 2.757(3) | 165(3) |
| O5–H5A→…O4$^2$ | 0.85(2) | 1.93(3) | 2.757(3) | 165(3) |

$^a$D = Donor, A = acceptor. For found and refined atoms the standard deviations are given. Symmetry relation: \(2 \rightarrow -x + 1, y, -z + 1\).
The cadmium compound 1 loses the methanol and some of the water of crystallization together with the ammine ligands during air-drying of the sample. The X-ray powder diffractogram of the dried sample is already substantially different from those of the calculated diffractogram from the single-crystal data (Fig. 11). Strong calculated peaks are clearly absent in the experimental diffractogram. Calculating the diffractogram without the methanol and water molecules does not improve the matching with the experimental curve so that the solvent loss apparently leads to considerable restructuring.

No mass losses were seen for MeOH in the TG/DTG curves with \( m/z \approx 32 \). Differential thermogravimetry (DTG, \( d\Delta m/dT \)) and thermogravimetry (TG, \( \Delta m \)) show four principal mass losses, which are all endothermic occasions from differential thermal analysis (DTA, \( \Delta T \)) (Fig. 12). The first weak TG step (peak temperature \( T_p = 61 \, ^\circ C \)) matches with the loss of the

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Hydrogen bonding interactions in 2(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-H(^+)A</td>
<td>D-H/Å</td>
</tr>
<tr>
<td>Intra-strand BINOL--BINOLAT:</td>
<td></td>
</tr>
<tr>
<td>O1-H1D--O4</td>
<td>0.88(6)</td>
</tr>
<tr>
<td>O3(^-)H3D--O2</td>
<td>0.75(6)</td>
</tr>
<tr>
<td>O5-H5B--O2</td>
<td>0.86(4)</td>
</tr>
<tr>
<td>O8-H8B--O4</td>
<td>0.81(4)</td>
</tr>
<tr>
<td>O7-H7A--O10</td>
<td>0.83</td>
</tr>
<tr>
<td>Ag-NH(^-)BINOL/BINOLAT:</td>
<td></td>
</tr>
<tr>
<td>N1-H1A--O8</td>
<td>0.90</td>
</tr>
<tr>
<td>N1-H1B--O1</td>
<td>0.90</td>
</tr>
<tr>
<td>N2-H2A--O7(^-)</td>
<td>0.90</td>
</tr>
<tr>
<td>N2-H2B--O4(^-)</td>
<td>0.90</td>
</tr>
<tr>
<td>N3-H3A--O6(^-)</td>
<td>0.90</td>
</tr>
<tr>
<td>N3-H3B--O2(^-)</td>
<td>0.90</td>
</tr>
<tr>
<td>N4-H4A--O5</td>
<td>0.90</td>
</tr>
<tr>
<td>N4-H4B--O3(^-)</td>
<td>0.90</td>
</tr>
<tr>
<td>EtOH--BINOL:</td>
<td></td>
</tr>
<tr>
<td>O6-H6a--O9(^+)</td>
<td>0.83</td>
</tr>
</tbody>
</table>

\( D = \) Donor, \( A = \) acceptor. For found and refined atoms the standard deviations are given. Symmetry relation: 1 = \( x + 1, y, z = x, y + 1, z = 2 \).
Intra-strand BINOL… BINOLAT:
- inter-strand
2
D
deficient compound would lead to
3

N2–H2A… O21 0.90 2.56 3.267(3) 136
N1–H1C… O3 0.90 2.31 3.036(3) 138
O6–H6A… O7 0.87(4) 1.88(4) 2.747(4) 179(5)

- intra-strand
BINOLAT2
furan and CO 2. The third and fourth step are not well
not allow for a measure of the relative amounts of dinaphtho-
BINOLAT. The intensity of the peaks in the mass spectra do
matches with the simultaneous loss of the BINOLAT 2
m
ammine ligands (MS-scan
m
Ag–NH3… BINOL/BINOLAT:
N2–H2C… O61 0.90 2.40 3.166(4) 143
N2–H2B… O43 0.90 2.13 2.972(3) 155
O3–H3A… O43

D–H… A
D–H/A Å
H… A/A Å
D–H… A/A Å
D–H… A/

Table 3 Hydrogen bonding interactions in 3°

<table>
<thead>
<tr>
<th>D–H… A</th>
<th>D–H/Å</th>
<th>H… A/Å</th>
<th>D–H/Å</th>
<th>D–H/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1–H1D--O4¹</td>
<td>0.72(3)</td>
<td>1.87(3)</td>
<td>2.579(2)</td>
<td>172(4)</td>
</tr>
<tr>
<td>O3–H3A--O4³</td>
<td>0.82(3)</td>
<td>1.82(3)</td>
<td>2.625(3)</td>
<td>169(3)</td>
</tr>
<tr>
<td>Ag–NH3…BINOLAT:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1–H1B…O1</td>
<td>0.90</td>
<td>2.25</td>
<td>3.102(3)</td>
<td>157</td>
</tr>
<tr>
<td>N1–H1C…O3</td>
<td>0.90</td>
<td>2.31</td>
<td>3.036(3)</td>
<td>138</td>
</tr>
<tr>
<td>N2–H2A–O4²</td>
<td>0.90</td>
<td>2.56</td>
<td>3.26(3)</td>
<td>136</td>
</tr>
<tr>
<td>N2–H2B–O4³</td>
<td>0.90</td>
<td>2.13</td>
<td>2.972(3)</td>
<td>155</td>
</tr>
<tr>
<td>H2O–BINOL:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O6–H6A…O7</td>
<td>0.87(4)</td>
<td>1.88(4)</td>
<td>2.747(4)</td>
<td>179(5)</td>
</tr>
</tbody>
</table>

° D = Donor, A = acceptor. For found and refined atoms the standard
deviations are given. Symmetry relations: 1 = x, y + 1, z; 3 =
-x, y + 1/2, -z + 1/2; 3' = -x, y - 1/2, -z + 1/2; 4 = x - 1/2,
-y - 1/2, -z.

remaining water (MS-trend-scan m/z = 18). The second TG
step (T_p = 119 °C) corresponds to the loss of the remaining
ammine ligands (m/z = 17). Starting from an only methanol-
deficient compound would lead to \( \Delta m_{\text{theor}} = 1.7\% \) for the loss of
H_2O and \( \Delta m_{\text{exp}} = 6.4\% \) for the loss of 4 NH_3 which is more
than the combined \( \Delta m_{\text{exp}} = 6.8\% \) for the first two steps. In
the third TG step (T_p = 290 °C) the two free BINOL molecules
(m/z = 286) are lost. The fourth TG step (T_p = 430 °C)
matches with the simultaneous loss of the BINOLAT^2-
 equivalent to its derivative dinaphtho[1,2-b:1',2'-d]furan^2-
(BINOLAT^2-–O^2- = m/z = 268) and carbon dioxide
(m/z = 44). The CO_2 may be formed by partial oxidation of
BINOLAT. The intensity of the peaks in the mass spectra do
not allow for a measure of the relative amounts of dinaphtho-
furan and CO_2. The third and fourth step are not well
separated, but their combined mass loss \( \Delta m_{\exp} = 77\% \) agrees
with the loss of two BINOL and a dinaphthofuran fragment
with combined \( \Delta m_{\text{theor}} = 79.7\% \). With respect to the BINOL/
BINOLAT loss the thermal behavior of 1 is very similar to
the one observed in the racemic analog [Cd(NH_3)_2]^2+(rac-
BINOLAT)^2-(rac-BINOL)_2.27 The residue was amorphous so
that it was not possible to make a powder measurement.
polarization microscope. At the surface of each individual crystal small crystal needles formed like prickles as a result of the heating (Fig. 14).

X-Ray powder measurements prove the amorphous nature of the heated crystals of 2 (Fig. 15). Lines from the calculated diffractogram based on the single-crystal data can no longer be seen in the experimental diffractogram after heating. Instead, new peaks have appeared which can be matched to the diffractogram of (S)-bi-1,1'-napthol and to elemental silver. The silver lines at 20 = 38.117 and 44.278° with a relative intensity of 100 and 40 are indexed to the (111) and to the (200) reflection, respectively. We assign the crystal "prickles" formed on the surface of the initial crystal needles to BINOL which is transported from the bulk material with the evaporating ethanol (and ammonia) (mp 208–210 °C for BINOL). When the heating is carried out in a very small closed container a liquid phase forms around the initial crystals which later dries to an amorphous BINOL solid after opening.

An elemental analysis of the heated sample of 2 (found C 70.79, H 3.73, N < 0.2% = exp. error) matches a calculation for (Ag~BINOLAT~)(BINOL) (C26H27AgO4, calc. C 70.70, H 4.01, N 0.00). An IR spectrum of the heated sample of 2 (νmax/cm⁻¹: 3508 m, 3485 m, 3429 m, 3053 w, 1617 m, 1595 m, 1507 m, 1468 m, 1437 w, 1424 w, 1381 m, 1345 m, 1317 m, 1271 m, 1253 m, 1219 m, 1181 m, 1147 s, 1125 m, 1072 m, 978 m, 950 m, 931 m, 863 m, 815 s, 776 m, 748 s, 677 w, 664 m, 626 w, 565 s, 489 w, 436 m, 421 m) agrees quite well with an IR of S-BINOL and some characteristic peaks for the original compound 2 were absent.

### Emission spectra of 1 and 2

The emission spectrum of 1 is different both to the emission spectrum of BINOL (Fig. 16) and to the spectrum of the racemic analog [Cd(NH₃)₆]²⁺(rac-BINOL)₂. The maximum at 300 nm, due to a vibronic side band for the S0–S1 system, is much more intense than in BINOL or the racemic analog. The maximum at 384 nm is close to the main maximum of 372 nm in BINOL and the racemic analog and is assigned to intraligand transitions. The third, strong maximum at 591 nm which is absent in the emission spectra of both BINOL and the racemic analog is attributed to a metal–ligand transition from the direct Cd-O-O'-BINOL chelate coordination in 1. The emission spectrum of the supramolecular compound 2 shows a major maximum at 363 nm with shoulders at 322, 348 and 478 nm (Fig. 16). There are two more smaller maxima at 530 and 608 nm. This emission spectrum is very similar to one of BINOL, where the major maximum at 372 nm has shoulders at 303, 393, 433 and 464 nm. The shoulder at 303 nm is a vibronic side band for the S₀-S₁ system. The major maxima at 388 and 372 nm, respectively, are assigned to intraligand transitions. The weak maxima at 530 and 608 nm may be metal–ligand transitions.

### Conclusions

The propensity for a hydrogen-bonded strand formation between BINOL and its deprotonated anion continued to show in the ammine-metal structures derived from chiral S-BINOL. This supramolecular strand formation was already earlier observed in the structures of [M(NH₃)₆]²⁺(rac-BINOLAT²⁻)(rac-BINOL)₂ (M = Ni or Cd, n = 6; M = Zn, n = 4). Crystals were again obtained from aqueous ammonium/alcohol solutions. The strand adapts when going from raceto S-BINOL by incorporating additional solvent molecules of crystallization, such as ethanol or water/methanol, to...
apparently compensate for a loss in hydrogen bonding between the R- and S-forms of BINOL.

Despite numerous attempts crystals from solutions of S-BINOL could, so far, only be grown with cadmium as a dicaticonic metal. With other M^{2+} cations, such as zinc or nickel under otherwise identical conditions, only powdery products were obtained from S-BINOL. With cadmium the formula now becomes \([\text{Cd}^{2+}(\text{S-BINOL})_2\text{-}k^2\cdot\text{O},\text{O}')(\text{NH}_3)_2](\text{S-BINOL})_2\cdot(\text{H}_2\text{O})(\text{MeOH})_2\) (I). As can be seen, another, concomitant change from the rac- to the S-BINOL structure of cadmium is the BINOL-k\(^2\cdot\text{O},\text{O}\) coordination in the latter, that is, a change in the cadmium coordination sphere. It will be interesting to know if this coordination mode persists in other (lanthanide) complexes with S-BINOL.\(^{42}\) An oxygen coordination of BINOLAT is hitherto mainly observed and structurally authenticated only with Pd\(^{41}\) and Pt.\(^{42}\) For each deprotonation, that is, for each negative charge of \(\text{S}^{1}\), a “free” BINOL is included in the supramolecular structure. Thus, the hydrogen-bonded BINOLAT-BINOL strand can in all cases, so far, be described by the general formula \((\text{BINOLAT})_2\text{-}\{\text{BINOL}\}\) for both rac- and S-forms. Furthermore, the BINOLAT charge is, so far, always found as \(n = 2\) for depositions and \(n = 1\) for the monocation Ag\(^+\). The intra- and inter-strand naphthyl arrangement exhibits only C-H–π interactions.\(^{43}\) There is no π-π stacking.\(^{44}\)

The chiral structures of 1, 2, and 3 crystallize in anacrinic (but not chiral), so-called Sohnke space groups.\(^{45}\)

### Experimental

Elemental analyses were obtained on a VarioEL from Elementaranalysensysteme GmbH. IR spectra (2-4 mg compound/300 mg KBr pellet) were measured on aBruker Optik FTIR 525. NMR spectra were collected on a Bruker ARX200 (200 MHz for \(^{1}H\)) with calibration against the residual protonated solvent signal (DMSO 2.52 ppm). S-BINOL was purchased from Fluka. rac-BINOL was prepared by the oxidative coupling of 2-naphthol through FeCl\(_3\)-oxidative coupling of 2-naphthol through FeCl\(_3\) \((20.16\,\text{mg})\) in an aqueous solution of ammonia (3 ml) was combined with a solution of Cd(NO\(_3\))\(_2\)-4H\(_2\)O (30.8 mg, 0.1 mmol) in MeOH (3 ml) was combined with a solution of Cd(NO\(_3\))\(_2\)-4H\(_2\)O (30.8 mg, 0.1 mmol) in MeOH (3 ml), hydrogenated in a Pd catalyst at 1 atm and 50 °C for 24h. The hydrogenated products were then isolated by column chromatography on silica gel with CH\(_2\)Cl\(_2\) as eluent.

### Synthesis

#### [Tetraammine-x\(^2\cdot\text{O},\text{O}\)-\(\text{S}^{1}\)-bi-2-naphtholate(2-)cadmium(II)]-bis[\text{S}^{1}\)-bi-2-naphtholate(bis(2-aminoethanol))\]

A solution of \(\text{S}^{1}\)-bi-2-naphtholate(2-) (28.6 mg, 0.1 mmol) in MeOH (3 ml) was combined with a solution of Cd(NO\(_3\))\(_2\)-4H\(_2\)O (30.8 mg, 0.1 mmol) in MeOH (3 ml) was combined with a solution of Cd(NO\(_3\))\(_2\)-4H\(_2\)O (30.8 mg, 0.1 mmol) in MeOH (3 ml) was combined with a solution of Cd(NO\(_3\))\(_2\)-4H\(_2\)O (30.8 mg, 0.1 mmol) in MeOH (3 ml), hydrogenated in a Pd catalyst at 1 atm and 50 °C for 24h. The hydrogenated products were then isolated by column chromatography on silica gel with CH\(_2\)Cl\(_2\) as eluent.

### General procedure for silver-BINOL compounds [\(\text{Ag}^{+}(\text{NH}_3)_2\)-\(\text{S}^{1}\)-bi-2-naphtholate(2-)]-\text{(BINOL)}\text{(solvent)}

A solution of AgNO\(_3\) (17.0 mg, 0.1 mmol) in an aqueous solution of ammonia (26%). The solution was allowed to evaporate slowly at room temperature. After several days crystals formed which were suitable for X-ray single crystal analysis.

### Diamminesilver(II)-[\(\text{S}^{1}\)-bi-2-naphtholate(1-)]-\(\text{S}^{1}\)-bi-2-naphtholate(2)-ethanol

A solution of AgNO\(_3\) (17.0 mg, 0.1 mmol) in an aqueous solution of ammonia (26%). The solution was allowed to evaporate slowly at room temperature. After several days crystals formed which were suitable for X-ray single crystal analysis.
on rac-BINOL. C_{62}H_{62}CdN_{4}O_{9} (759.64; calc: C 64.49, H 5.15, N 3.67; found C 64.50, H 4.97, N 3.73%.

Diammine-silver(I)-([1,1'-bi-2-naphtholate]-(S,S')-BINOL) (3). Colorless plates, yield 29.0 mg, 76% based on rac-BINOL. C_{62}H_{62}CdN_{4}O_{9} (781.63; calc C 64.69, H 5.15, N 3.67; found C 64.50, H 4.97, N 3.73%.

Acknowledgements

We gratefully acknowledge financial support by the University of Freiburg. We thank Dr Martin Ade for helpful discussions.

References

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