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ARTICLE

Supramolecular Ammine-Copper *rac*-BINOLAT Salts through in-situ *R*- or *S*-BINOL Racemization

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Dedicated to Prof. Manfred Scheer on the Occasion of his 65th Birthday

Abstract. The molecule *rac*-1,1′-binaphthalene-2,2′-diol (*rac*-1,1′-bi-2-naphthol, *rac*-BINOL) shows a propensity for supramolecular, charge-assisted O–H···O⁻ hydrogen-bonded strand formation when crystallized with its deprotonated form $BINOLAT^{2-}$ and Cu^{2+} in conc. ammonia. The naphthyl-paneled cavities in the $\{(rac\text{-}BINOLAT^{2-})(rac\text{-}BINOL)_2\}$ strands host the $[Cu(NH_3)_5]^{2+}$-guest cation through second-sphere N–H···O hydrogen bonding in the structure of $[Cu(NH_3)_5]^{2+}(rac\text{-}BINOLAT^{2-})(rac\text{-}BINOL)_2$. Decreasing the copper(II) and ammonia concentrations in the crystallization leads to $\{(rac\text{-}BINOLAT^{2-})(rac\text{-}BINOL)\}$ strands, in which *rac*-$BINOLAT^{2-}$ coordinates to two copper(II) atoms in the structure of $[Cu(NH_3)_2(\mu\text{-}rac\text{-}BINOLAT^{2-}\text{-}\kappa^2O,O':\kappa O)]_2(rac\text{-}BINOL)_2$. In the $\{Cu^{2+}(NH_3)_2\}$ moiety two BINOLAT-oxide atoms act as bridging ligands. Both copper structures could be obtained by using the racemic *rac*-BINOL or the enantiomeric *R*- or *S*-BINOL, through an in-situ racemization of the latter.

Introduction

The C_2-symmetric, axially chiral molecule 1,1′-binaphthalene-2,2′-diol (1,1′-bi-2-naphthol or BINOL)[1] is well known in asymmetric catalysis,[2,3] and for chiral recognition processes.[4] Thereby, BINOL functions as an auxiliary molecule or ligand to a catalytic metal atom in the asymmetric transformation.

In the field of crystal engineering ,[5,6] enantiomeric or racemic BINOL (including its deprotonated BINOLAT form) has been used for the construction of (chiral) superstructures with $Co(\eta^5\text{-}C_5H_5)_2^+$ or alkali metal cations,[7,8] with volatile organic guests (1,4-dioxane, morpholine, dimethylsulfoxide, acetone and tetrahydrofuran),[9] with prochiral guests (α,β-unsaturated compounds, piperazinedione derivatives),[10] with 2,2′-bipyridine and naphthodiazine,[11] or with benzoquinone and aromatic hydrocarbons.[12]

We had investigated the supramolecular organization of *rac*-BINOL and its dianion ($BINOLAT^{2-}$) as chiral building blocks. The naphthyl-paneled cavities in O–H···O⁻ hydrogen-bonded $\{(BINOLAT^{2-})(BINOL)_2\}$ strands act as hosts and can accommodate $[M(NH_3)_n]^{2+}$ cations (M = Ni or Cd, $n = 6$ or M = Zn, $n = 4$) as guests through second-sphere N–H···O hydrogen bonding in the structures of $[M(NH_3)_n]^{2+}(rac\text{-}BINOLAT^{2-})(rac\text{-}BINOL)_2$. The ammine-metal complex can be an octahedron with $[Ni(NH_3)_6]^{2+}$ and $[Cd(NH_3)_6]^{2+}$ or a tetrahedron with $[Zn(NH_3)_4]^{2+}$ thereby showing the adaptability of the cavity (Scheme 1a).[13]

With enantiomeric *S*-BINOL, the cavities from the *racemic* structure (Scheme 1a), which are preserved in the $\{(S\text{-}BINOLAT^{2-})(S\text{-}BINOL)_2\}$ strand, are filled with the Cd cations albeit as a $Cd(NH_3)_4$ fragment (Scheme 1b). The change in hydrogen bonding between *S*-BINOL and *S*-BINOLAT in the now non-centrosymmetric structure brings with it a coordination of two oxygen atoms of $BINOLAT^{2-}$ to cadmium in the structure $[Cd(S\text{-}BINOLAT^{2-}\text{-}\kappa^2O,O')(NH_3)_4](S\text{-}BINOL)_2(H_2O)(MeOH)_2$.[14]

Herein we extend our investigations on BINOL as a supramolecular synthon with Cu^{2+} in ammoniacal solution. Furthermore we discovered an in-situ racemization of enantiomeric *R*- or *S*-BINOL in the presence of copper(II) and ammonia (Scheme 2).

Results and Discussion

Crystallization of copper(II) with BINOL from an ammoniacal water/methanol solution gave ammine-copper salts with doubly deprotonated 1,1′-bi-2-naphthol (as $BINOLAT^{2-}$) (see Supporting Information for synthetic details). The salts crystallized with neutral BINOL. Remarkably, when using single enantiomers of *R*- or *S*-BINOL the crystals only contained the

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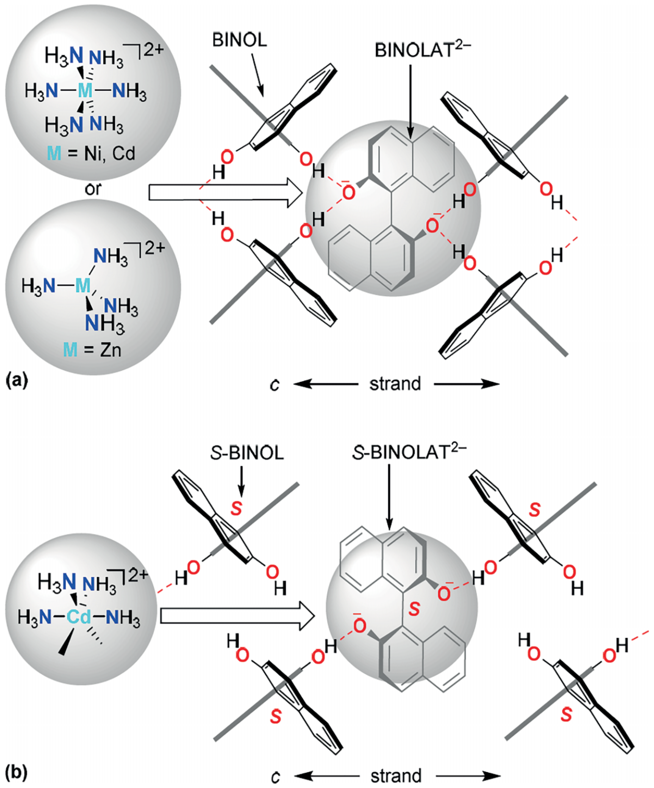
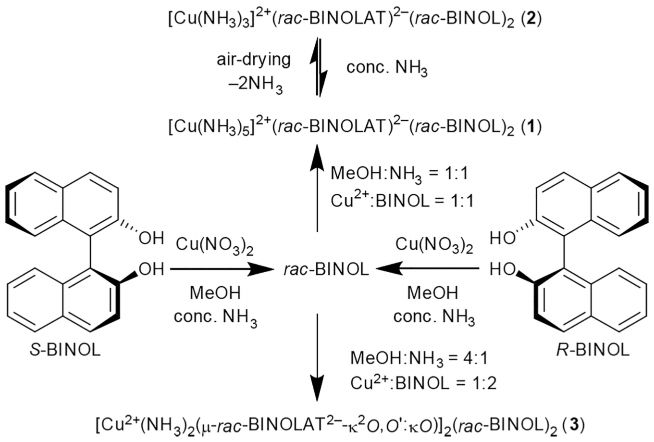


Scheme 1. Schematic presentation of the {(*rac*-BINOLAT^{2-})(*rac*-BINOL)$_2$} strand in the structures of $[M(NH_3)_n]^{2+}$(*rac*-BINOLAT^{2-})(*rac*-BINOL)$_2$ and the inclusion of the ammine-metal counter-cations (M = Ni or Cd, n = 6 or M = Zn, n = 4).



Scheme 2. Schematic presentation of the crystallization of *R*-BINOL, *S*-BINOL, or *rac*-BINOL with copper(II) nitrate from an ammonia/methanol solution.

racemate in $[Cu(NH_3)_5]^{2+}$(*rac*-BINOLAT^{2-})(*rac*-BINOL)$_2$ (**1**) and in $[Cu^{2+}(NH_3)_2(\mu$-*rac*-BINOLAT^{2-}-$\kappa^2O,O':\kappa O)]_2$(*rac*-BINOL)$_2$ (**3**). When starting from *rac*-BINOL, the same products **1** and **3** were obtained as from the enantiomeric forms. The difference in composition between **1** and **3** was due to a change in copper(II) and ammonia concentrations, both being lower for **3** (cf. Scheme 2).

Compound **1** was obtained as green crystals (Figure S1, Supporting Information), compound **3** as brown crystals (Figure S2, Supporting Information), both from methanol/aqueous ammonia.

The racemization of *R*- or *S*-BINOL was initially verified through single-crystal X-ray diffraction with both **1** and **3** crystallizing in centrosymmetric space groups ($C2/c$ and $P\bar{1}$, respectively, see Table S1, Supporting Information, for crystal data and refinement details).

Crystal Structure of $[Cu(NH_3)_5]^{2+}$(rac-BINOLAT^{2-})(rac-BINOL)$_2$ (1)

The supramolecular O–H···O$^-$ hydrogen-bonding organization of *rac*-1,1′-bi-naphthol (BINOL) and its dianion (BINOLAT^{2-}) together with the second-sphere N–H···O hydrogen-bonding interaction from the pentaamminecopper(II) complex $[Cu(NH_3)_5]^{2+}$ (Figure 1, Scheme 3) is essentially identical to the known structures of $[M(NH_3)_n]^{2+}$(*rac*-BINOLAT^{2-})(*rac*-BINOL)$_2$ (M = Zn, n = 4; M = Ni, Cd, n = 6) (cf. Scheme 1).[12]

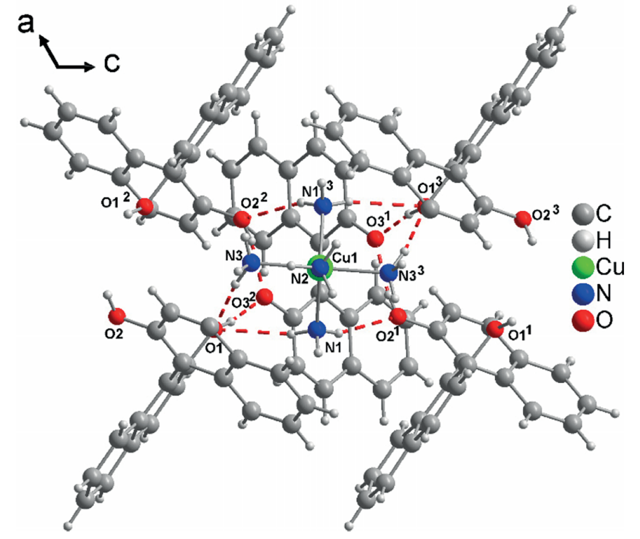
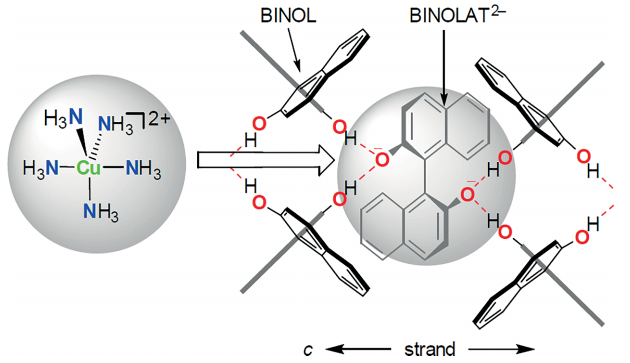


Figure 1. Section of the molecular packing in $[Cu(NH_3)_5]^{2+}$(*rac*-BINOLAT^{2-})(*rac*-BINOL)$_2$ (**1**) with hydrogen bonds indicated as red dashed lines; see Tables S2 and S3 (Supporting Information) for bond and angle details; symmetry relations: 1 = x, 1 $-y$, 0.5 + z; 2 = $-x$, 1 $-$ y, $-z$; 3 = $-x$, y, 0.5$-z$.



Scheme 3. BINOLAT/BINOL hydrogen-bonding arrangement, paneling and cavity formation in the structure of $[Cu(NH_3)_5]^{2+}$(*rac*-BINOLAT^{2-})(*rac*-BINOL)$_2$ (**1**) (cf. Scheme 1).

The copper(II) cation in compound **1** is in a weakly distorted trigonal-bipyramidal coordination sphere of the five ammine ligands. For the pentaamminecopper complex $[Cu(NH_3)_5]^{2+}$ in **1** an Addison parameter of $\tau = 0.94$ was found with the two largest angles N3–Cu1–N3^3 = 179.5° and N1–Cu1–N1^3 = 123.4° (Table S2, Supporting Information) ($\tau = 1$ for an ideal trigonal bipyramid and $\tau = 0$ for an ideal square pyramid).[15]

As seen before in $[M(NH_3)_n]^{2+}$(*rac*-BINOLAT^{2-}) (*rac*-BINOL)$_2$ (M = Ni, $n = 6$; Zn, $n = 4$; Cd, $n = 6$)[23] the packing of the molecular building blocks in **1** appears to be controlled by the charge-assisted O–H···O$^-$ hydrogen bonding between BINOL and BINOLAT (Table S3, Supporting Information). Each naphthoxide oxygen atom of the completely deprotonated 1,1′-bi-2-naphtholate moiety (BINOLAT) is an acceptor of two hydrogen bonds from an OH group of each of the two 1,1′-bi-2-naphthol molecules. This hydrogen-bonding mode gives rise to a BINOLAT/BINOL strand formation along *c* (Figure 1). These strands are the same for the different sizes (Ni vs. Cd in $[M(NH_3)_6]^{2+}$) and shapes of the ammine-metal cation (octahedral for Ni and Cd, tetrahedral for Zn and trigonal bipyramidal for Cu). The intra-strand naphthyl arrangement exhibits only C–H···π interactions.[16] There is no π–π stacking.[17]

The cavities, which are created within the BINOLAT/BINOL strand through the paneling of the naphthyl rings, contain the $[Cu(NH_3)_5]^{2+}$ fragments (Scheme 3) which are connected to the BINOLAT/BINOL strand through N–H···O hydrogen bonding (Table S3, Supporting Information).

The outside of the strands is hydrophobic/lipophilic and neighboring strands are hexagonally packed along *a* and *b* with the inter-strand packing dictated by C–H···π interactions.[15] Each strand contains both enantiomeric forms of the racemic BINOL mixture. For both the BINOLAT and the BINOL moiety, the *R* and *S* enantiomer alternate along the strand in the *c* direction.

The presence of ammine vs. aqua ligands on the copper(II) cation in **1** was evident from elemental analysis (see Experimental Section in Supporting Information) and further proven by simultaneous differential thermoanalysis, thermogravimetry and mass spectrometry (DTA-TG-MS). The TG and DTG curves show three mass losses, all of them are accompanied with endothermic events in the DTA curves (Figure 2). The first TG step (peak temperature: T_p = 92 °C) is due to the loss of two of the five ammine ligands (MS-trend-scan m/z = 17; Δm_{exp}: 3.6, Δm_{theo}: 3.4 %). The second TG step (T_p = 131 °C) matches with the loss of the other three ammine ligands (Δm_{exp}: 4.9, Δm_{theo}: 5.1 %). In the last TG step (T_p = 328 °C) a BINOL molecule (m/z = 286) and two of its dinaphtho[1,2-*b*:1′,2′-*d*]furan derivatives (m/z = 268)[18] are lost simultaneously ($\Delta m_{exp.}$: 80.8, Δm_{theo}: 81.8 %).

One characteristic of $[Cu(NH_3)_5]^{2+}$(*rac*-BINOLAT^{2-})(*rac*-BINOL)$_2$ was that the original green crystals (Figure S1, Supporting Information) turned into a brown powder after drying (Figure S3, Supporting Information). By addition of concentrated aqueous ammonia solution to the brown powder a green powder with the analytical data of **1** could be regenerated (Scheme 2). The brown-to-green conversion appears to be a solid-to-solid transformation as the microscopic observation revealed no dissolution of the brown powder in concentrated ammonia. Elemental analysis and investigation of the brown powder by simultaneous differential thermoanalysis, thermogravimetry, and mass spectrometry (DTA-TG-MS, Figure S4, Supporting Information) indicated two less NH_3 ligands when compared to **1**. Thus, the brown powder was assigned the formula $[Cu(NH_3)_3]^{2+}$(*rac*-BINOLAT^{2-})(*rac*-BINOL)$_2$ (**2**). Crystallization attempts of **2** failed.

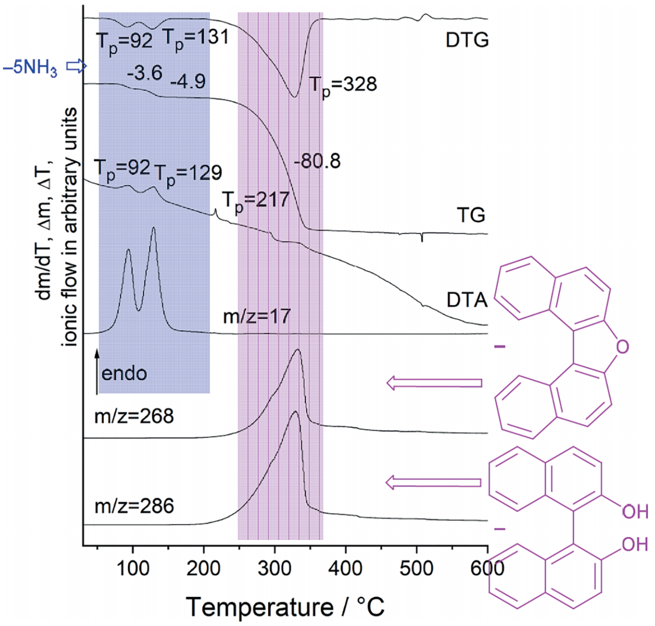


Figure 2. DTG, TG, DTA, and MS-trend-scan curve for $[Cu(NH_3)_5]^{2+}$(*rac*-BINOLAT^{2-})(*rac*-BINOL)$_2$ (**1**) (m/z = 17: NH_3; m/z = 268: dinaphthofuran and m/z = 286: BINOL); values refer to the mass loss in % (TG) and to the peak temperature (T_p) in °C (DTG).

Crystal Structure of $[Cu^{2+}(NH_3)_2(\mu\text{-}rac\text{-}BINOLAT^{2-}\text{-}\kappa^2O,O'{:}\kappa O)]_2(rac\text{-}BINOL)_2$ *(3)*

While the ammonia-depleted compound **2** could not be crystallized, a crystalline ammonia-deficient compound **3**, when compared to **1**, could be obtained by lowering the copper and ammonia concentration (Scheme 2). The ammonia-depleted compound **2** and the crystals of compound **3** have a similar brown color. In view of the different Cu:NH_3 ratio of 1:3 in **2** and 1:2 in **3** the coordination environment cannot be fully identical. The copper(II) coordination environment in **3** was structurally elucidated as $\{CuN_2O_3\}$ (see below). Thus, for compound **2** an environment of $\{CuN_3O_2\}$ may be assumed.

The coordination sphere of the copper(II) atom in compound **3** is a weakly distorted square pyramid. The copper(II) atom is coordinated by two *cis*-positioned ammine ligands and two *cis*-positioned bridging BINOLAT oxygen atoms. These four atoms form the base of the square pyramid. The second oxygen atom of a bridging BINOLAT coordinates in the apical position with a long Cu–O2 bond (Figure 3). A value of $\tau = 0.15$ was found (based on N1–Cu–O1 = 172° and N2–Cu–O1^6 = 163°). A dinuclear $\{CuN_2O_3\}_2$ entity is formed through the bridging action of one oxide atom in each BINOLAT ligand (Figure 3).

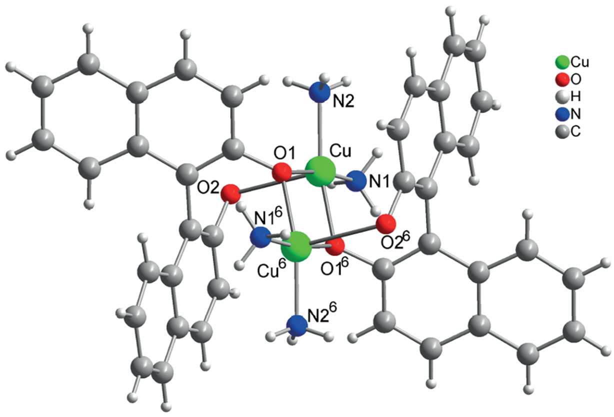
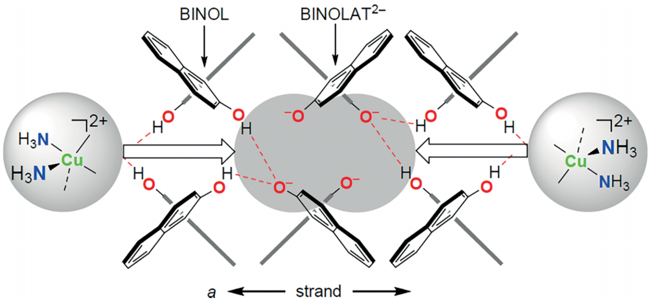


Figure 3. Centrosymmetric dinuclear copper unit in $[Cu^{2+}(NH_3)_2(\mu$-*rac*-BINOLAT^{2-}-κ^2O,O':$\kappa O)]_2$(*rac*-BINOL)$_2$ (**3**); see Tables S4 and S5 (Supporting Information) for bond and angle details; symmetry relation: 6 = –x, -y, 2 –*z*.

The packing of the molecular building blocks appears again to be controlled by the O–H···O$^-$ hydrogen bonding between BINOL and BINOLAT (Table S5, Supporting Information). The naphthoxide oxygen atom of BINOLAT which binds only to one copper atom is an acceptor of two O-H···O hydrogen bonds from a BINOL OH groups. Each of these two BINOL-OH groups is also an acceptor of a N–H···O hydrogen bond (Table S5, Figure S6, Supporting Information).

This hydrogen-bonding mode gives rise to a BINOLAT/BINOL strand formation along *a* (Scheme 4, Figure S6). The intra-strand naphthyl arrangement exhibits only C–H···π interactions.[27] There is no π–π stacking.[28]



Scheme 4. BINOLAT/BINOL hydrogen-bonding arrangement, paneling and cavity formation in the structure of $[Cu^{2+}(NH_3)_2(\mu$-*rac*-BINOLAT^{2-}-κ^2O,O':$\kappa O)]_2$(*rac*-BINOL)$_2$ (**3**).

The 1:1 BINOLAT:BINOL ratio in **3** (compared to 2:1 in **1**) joints two adjacent cavities in **1** to a larger one, which then contain the bis(diamminecopper) unit (Scheme 4). This dinuclear unit is connected with the BINOLAT/BINOL strand through N–H···O hydrogen bonding (Table S4, SI).

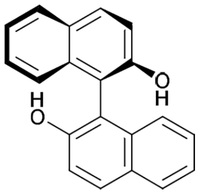
The outside of the strands is again hydrophobic/lipophilic and neighboring strands are hexagonally packed along *b* and *c* with the inter-strand packing dictated by C–H···π interactions (Figures S7 and S8, Supporting Information).[27]

As in **1** also in **3** each strand contains both enantiomeric forms of the racemic BINOL mixture. For both the BINOLAT and the BINOL moiety the *R* and *S* enantiomer alternate along the strand in the *a* direction.

Racemization of BINOL

The racemization of enantiomeric BINOL could be observed with copper(II) nitrate in the presence of ammonia but not with transition metal salts of cadmium(II), nickel(II), zinc(II), or silver(I). For cadmium(II) and silver(I) in the presence of ammonia the enantiopure compounds of [Cd(*S*-BINOLAT^{2-}-κ^2O,O')$(NH_3)_4$](*S*-BINOL)$_2$$(H_2O)$(MeOH)$_2$, $[Ag(NH_3)_2]^+$(*S*-BINOLAT$^-$)(*S*-BINOL)(EtOH) and $[Ag(NH_3)_2]^+$(*S*-BINOLAT$^-$)(*S*-BINOL)$(H_2O)_2$(MeOH) are obtained instead as it was reported earlier.[13] We also verified that both, copper(II) and ammonia were necessary for the racemization. The racemization of *R*-BINOL could not be observed with only copper(II) or only ammonia present in the *R*-BINOL solution at room temperature.

Meca et al. showed that the racemization of BINOL occurs over an *anti-Ci* transition state (Scheme 5). The density functional theory (DFT) B3LYP 6-31G(d,p) calculated relative energy of the transition structure of 158 kJ·mol^{-1} agrees with the experimental values (155.5 to 158 kJ·mol^{-1}). The energy barrier depends on the level of theory. (AM1 and PM3 underestimate with 129 and 144 kJ·mol^{-1}, respectively, and HF highly overestimates with 210 kJ·mol^{-1} the height of the rotational barrier). This centrosymmetric transition state structure has both hydroxy groups in a syn conformation with short (O)H···C8' and O···H8' distances of 2.09 and 2.34 Å, respectively.[19] The energy barrier of the transition state is mainly due to the nonplanar geometries of naphthyl rings.



Scheme 5. *anti-Ci*-transition state of the BINOL racemization according to theoretical studies.[18,19]

A recent study by *Tkachenko* et al. used three DFT methods (PBE0, B3LYP and TPSSh) with the Pople augmented basis set 6-311+G* plus the implemented MP4/cc-pVDZ//B3LYP/6-311+G* level of theory. The study confirmed that the racemization of BINOL passes through a preferred *anti-Ci* transition state with an energy of 164 kJ/mol and a strong deformation of the aromatic system.[20]

While BINOL has considerable stability under neutral conditions, it is often stated to readily racemize in both acidic and basic solutions.[2,21] In acids, the protonation of the C1 atom gives a cationic species in which the naphthyl rings can rotate about a C(sp2)-C(sp3) bond. In bases, deprotonation of the hydroxyl groups yields a dianion with possible rotation about the C1–C1' bond with decreased steric hindrance. In the apparent first reference to the racemization in basic solution, (–)-(*S*)-BINOL racemized 69 % in butanol which was 0.67

mol·L^{-1} in KOH at 118 °C for 23 h.[22] A later study reported for the base-induced racemization, that the enantiomeric excess of (–)-BINOL decreased from 99 % to 0 % in boiling 5 % aqueous NaOH over 12 h.[23] The estimated experimental enantiomerization barriers from these conditions are 135.3 kJ•mol^{-1} and 122.3 kJ•mol^{-1}, respectively.[24] BINOL does not show any sign of racemization on heating in neutral water at 100 °C for 24 h.

The enantiomerization transition barrier (corrected for zero-point energy) at the B3LYP/6-31G(d) level of theory was calculated for neutral BINOL as 158.4 kJ•mol^{-1} for the monoanion BINOL^{1-} as 167.0 kJ•mol^{-1} and for the dianion BINOL^{2-} (denoted as BINOLAT^{2-} in this work) as 113.4 kJ/mol. The later value corresponds to about 120 kJ•mol^{-1} at 100 °C. Following the process of racemization experimentally by enantioselective chromatography gave a barrier for the dianion of 136.2 ± 0.5 kJ•mol^{-1} at 385.15 K (112 °C) in butan-1-ol and of 130–134 kJ•mol^{-1} in water at 372.25 K (100 °C).[24]

Typically, a racemization of an enantiomeric compound seems to be disadvantageous, but in some cases induced racemizations can be turned into an advantage. This is the case for processes that utilize the separation of a desirable enantiomer from a racemic mixture through resolution. Such a separation inherently yields about 50 % of the undesirable enantiomer and only 50 % for the wanted one. Hence, recycling of the undesirable isomer via a racemization is then economically advantageous in order to enrich the desired product step-by-step. Controlled racemization requires appropriate techniques which must be available.[25,26]

Subsequent to our above findings on the racemization of 1,1′-bi-2-naphthol by copper(II) under ammoniacal conditions, we determined the rate constant and activation energies for the process. The change of the optical activity of a methanol *R*-BINOL solution (30.0 mg, 0.105 mmol in 1.5 mL) upon addition of copper(II) nitrate (2.54 mg, 0.0105 mmol) in aqueous ammonia (1.5 mL, 26 %) was measured at different temperatures (see Supporting Information for details). The changes of the optical activity α gave the rate constant k_1 at different temperatures from which the Arrhenius plot of lnk_1 vs. reciprocal absolute temperature (1/T) (Figure S9, Supporting Information) yielded an activation energy of 99 kJ•mol^{-1}. This value is smaller than what was experimentally found and calculated for the dianion in basic solution alone.[24] Thus, an additional role of the Cu^{2+} ion can be assumed, possibly through a weak coordination which aids the racemizing rotation about the C1–C1’ bond. Since Cu^{2+} is known for not being redox-inert in many reactions, a radical process may be involved in the racemization. A brief density functional theoretical modeling attempt of a reaction coordinate in which BINOLAT^{2-} is coordinated by a metal atom (precisely M = Cu^{2+}, Ni^{2+} and Zn^{2+}) and the metal atom is additionally coordinated by two ammine ligands (either planar or tetrahedral) did not give a transition state along proposed reaction coordinate (see Supporting Information for details). There was no difference for (active) Cu^{2+} vs. non-active Ni^{2+} and Zn^{2+} along the investigated reaction coordinate.

Conclusions

The naphthyl-paneled cavities formed in the hydrogen-bonded (*rac*-BINOLAT^{2-})(*rac*-BINOL)$_2$ strands act as host for metal complex counter cations: $[\mathrm{Cu(NH_3)_5}]^{2+}$ in the structure of $[\mathrm{Cu(NH_3)_5}]^{2+}$(*rac*-BINOLAT^{2-})(*rac*-BINOL)$_2$ or $\{\mathrm{Cu^{2+}(NH_3)_2}\}$ in $[\mathrm{Cu^{2+}(NH_3)_2}(\mu\text{-}rac\text{-BINOLAT}^{2-}\text{-}\kappa^2O,O'\text{:}\kappa O)]_2(rac\text{-BINOL})_2$. While the $[\mathrm{Cu(NH_3)_5}]^{2+}$-guest cation is accommodated through second-sphere N–H···O hydrogen bonding, the $\{\mathrm{Cu^{2+}(NH_3)_2}\}$ moiety is coordinated by oxide atoms from BINOLAT. At the same time the reaction conditions in methanol/aqueous ammonia induce an in-situ racemization when *R*- or *S*-BINOL are used as reagents. The products contain a racemic BINOL mixture and are identically obtained from *rac*-BINOL. Noteworthy, the quantitative BINOL racemization takes place at room temperature in the presence of Cu^{2+} (but not with Ni^{2+}, Zn^{2+}, Cd^{2+} or Ag^{+}). Such a facile induced racemization could allow the recycling of an unwanted enantiomer of BINOL or its derivatives.

Supporting Information (see footnote on the first page of this article): Synthesis and analysis, crystal data and refinement details, crystal photographs, DTG, TG, DTA and MS-trend-scan curve for **2**, lists with bond lengths and angles and hydrogen-bonding interactions, racemization of *R*-BINOL.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1975329, CCDC-1975330, CCDC-1975331, and CCDC-1975332 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Keywords: 1,1′-Binaphthalene-2,2′-diol; 1,1′-Bi-2-baphthol; BINOL; Racemization; Copper

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