

Enantiospecific Syntheses of Copper Cubanes, Double-Stranded Copper/Palladium Helicates, and a (Dilithium)–Dinickel Coronate from Enantiomerically Pure Bis-1,3-diketones—Solid-State Self-Organization Towards Wirelike Copper/Palladium Strands**

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Dedicated to Professor Ulrich Zenneck on the occasion of his 60th birthday

Abstract: Enantiomerically pure, vicinal diols **1** afforded in a two-step synthesis (etherification and subsequent Claisen condensation) chiral bis-1,3-diketones $H_2L^{(S,S)}$ (**3a–c**) with different substitution patterns. Reaction of these C_2 -symmetric ligands with various transition-metal acetates in the presence of alkali ions generated distinct polynuclear aggregates **4–8** by diastereoselective self-assembly. Starting from copper(II) acetate monohydrate and depending on the ratio of transition-metal ion to alkali ion to ligand, chiral tetranuclear copper(II) cubanes (C,C,C,C -[Cu₄(L^(S,S))₂(OMe)₄] (**4a–c**) or dinuclear copper(II) helicates (P -

[Cu₂(L^(S,S))₂] (**5**) could be synthesized with square-pyramidal and square-planar coordination geometry at the metal center. In analogy to the last case, with palladium(II) acetate double-stranded helical systems (P -[Pd₂(L^(S,S))₂] (**6,7**) were accessible exhibiting a linear self-organization of ligand-isolated palladium filaments in the solid state with short inter- and intramolecular metal distances. Finally, the introduction of hexacoordinate

nickel(II) in combination with lithium hydroxide monohydrate and chiral ligand $H_2L^{(S,S)}$ (**3a**) allowed the isolation of enantiomerically pure dinuclear nickel(II) coronate [(Li·MeOH)₂C-{(Δ,Δ)-Ni₂(L^(S,S))₂(OMe)₂}] (**8**) with two lithium ions in the voids, defined by the oxygen donors in the ligand backbone. The high diastereoselectivity, induced by the chiral ligands, during the self-assembly process in the systems **4–8** could be exemplarily proven by circular dichroism spectroscopy for the synthesized enantiomers of the chiral copper(II) cubane **4a** and palladium(II) helicate **6**.

Keywords: chirality • circular dichroism • copper • helical structures • nickel

Introduction

Over the past two decades, major efforts were undertaken to the metal-directed self-assembly^[1] of highly organized architectures (catenanes, rotaxanes, knots, grids, ladders, racks,

molecular squares and boxes, cubes, helicates, one- to three-dimensional networks etc.). In addition to their appealing structural design, the synthesis of these high-nuclearity coordination complexes of transition metals is stimulated by their electronic and magnetic properties, which predestine them as metalloenzyme models,^[2] nanoscale catalysts and containers,^[3] quantum computing components,^[4] and molecular magnets.^[5] In the last case, it is an interesting challenge to create chiral magnets, presenting at the same time magnetic circular dichroism (Faraday effect), natural circular dichroism (Cotton effect), and therefore possible cross-effects.^[6] One synthetic approach, leading to these chiral supramolecular architectures, is the combination of suitably designed enantiomerically pure organic ligands and metal ions,^[7] which we used earlier for the diastereoselective synthesis of copper(II) cubanes.^[8]

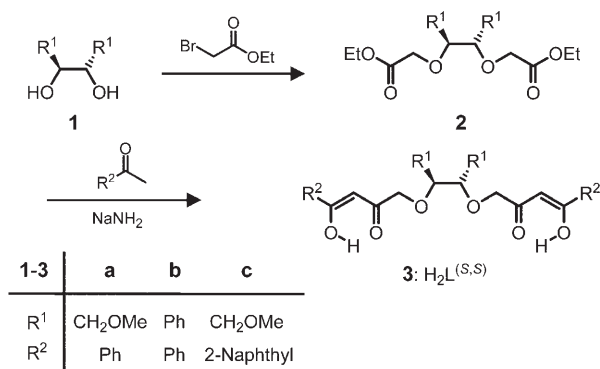
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Results and Discussion

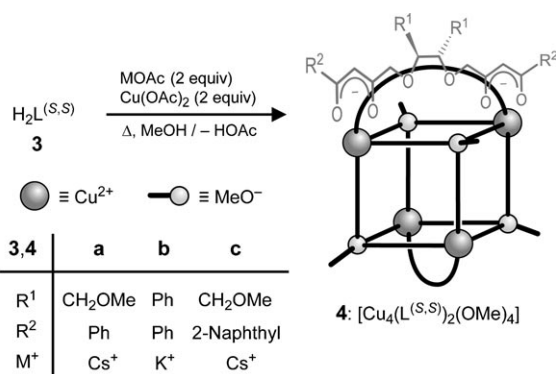
In the course of our ongoing studies on supramolecular coordination chemistry, we developed a stereospecific synthesis for the copper(II) cubanes (C,C,C,C) -[Cu₄(L^(S,S))₂(OMe)₄] (**4a**) and (A,A,A,A) -[Cu₄(L^(R,R))₂(OMe)₄] (*ent*-**4a**), starting from the chiral bis-1,3-diketones H₂L^(S,S) (**3a**) or H₂L^(R,R) (*ent*-**3a**) through diastereoselective self-assembly.^[8] Compared to earlier results,^[9] the presence of chiral centers in the ligand appeared to be responsible for the transition from a double-stranded copper(II) coronate to a copper(II) cubane substructure. To evaluate, if we have found a general method for the synthesis of chiral cubanes, enantiomerically pure and differently substituted H₂L^(S,S) (**3**) ligands,^[10] in which the chirality is incorporated in the spacer backbone, were generated from $(2S,3S)$ -1,4-dimethoxy-2,3-butanediol (**1a**), derived from L-tartaric acid,^[11] or (S,S) -(-)-hydrobenzoin (**1b**). Thus, etherification of diols **1** with ethyl bromoacetate was achieved in the presence of sodium hydride to afford diesters **2**. Subsequent Claisen condensation of **2** with sodium enolates, from acetophenone or 2-acetonaphthone and sodium amide, led to C₂-symmetric H₂L^(S,S) (**3**) (Scheme 1).^[12]



Scheme 1. Synthesis of the enantiomerically pure bis-1,3-diketones H₂L^(S,S) (**3**).

Reaction of one equivalent of **3a** with two equivalents of cesium acetate, followed by addition of two equivalents of copper(II) acetate monohydrate, resulted in the formation of (C,C,C,C) -[Cu₄(L^(S,S))₂(OMe)₄] (**4a**) in a yield of 84% (Scheme 2). Similarly, (A,A,A,A) -[Cu₄(L^(R,R))₂(OMe)₄] (*ent*-**4a**) was prepared from H₂L^(R,R) (*ent*-**3a**) and characterized by X-ray diffraction analysis.^[8,13] In addition, reaction of one equivalent of H₂L^(S,S) (**3b,c**) with two equivalents of alkali acetate and subsequent addition of two equivalents of copper(II) acetate monohydrate resulted in the formation of (C,C,C,C) -[Cu₄(L^(S,S))₂(OMe)₄] (**4b,c**) in yields of 90 and 82%, respectively (Scheme 2).^[14,15]

Cubane **4b** is isostructural with **4a**, exists as a single enantiomer, crystallizes in the chiral monoclinic space group C₂, and possesses a [Cu₄(μ₃-O)₄] cubane core unit^[16] consisting of two interpenetrating tetrahedra: one made up of four copper ions and one of four μ₃-OMe ligands. The metal-



Scheme 2. Synthesis and schematic presentation of (C,C,C,C) -[Cu₄(L^(S,S))₂(OMe)₄] (**4a-c**), starting from H₂L^(S,S) (**3a-c**).

metal separations in **4b** are 2.97 (Cu1–Cu1'), 3.25 (Cu1–Cu2), and 3.29 Å (Cu1–Cu2'). Each copper ion has approximate square-pyramidal coordination, with a total of five oxygen donors (two μ₁-O ions from the ligand and three μ₃-OMe donors). Consequently, the two hexadentate ligand bridge opposite edges of the copper tetrahedron (Figure 1).^[17,18]

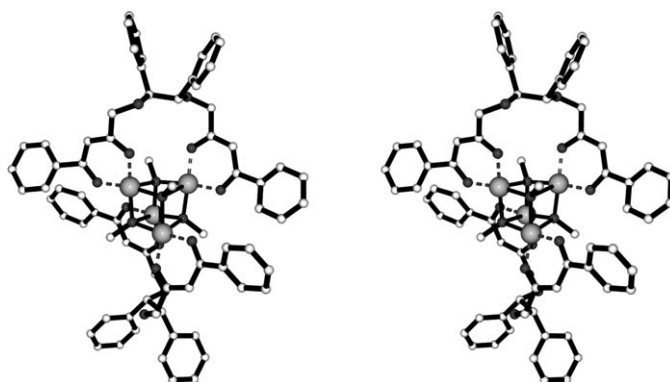


Figure 1. Stereoview of copper(II) cubane **4b**. C white, O dark grey, Cu grey; disorder and hydrogen atoms omitted for clarity.

The circular dichroism (CD) measurements of copper(II) cubanes **4a** and *ent*-**4a** in dichloromethane further confirm the opposite ground-state chirality and the enantiomeric nature of these complexes. The CD spectrum of (C,C,C,C) -[Cu₄(L^(S,S))₂(OMe)₄] (**4a**) exhibits two negative Cotton effects at λ_{max} = 415 and 646 nm and a positive dichroic signal centered at λ_{max} = 764 nm (dichroic crossover point at λ = 714 nm), while *ent*-**4a** shows Cotton effects of the opposite sign at the same wavelengths (Figure 2, top).

Whereas reaction of one equivalent of H₂L^(S,S) (**3b**) with two equivalents of potassium acetate and two equivalents of copper(II) acetate monohydrate resulted in the formation of (C,C,C,C) -[Cu₄(L^(S,S))₂(OMe)₄] (**4b**) (Scheme 2), unexpectedly, reaction of H₂L^(S,S) (**3b**) with five equivalents of potassium acetate and one equivalent of copper(II) acetate monohydrate yielded the double-stranded helicate (*P*)-[Cu₂-

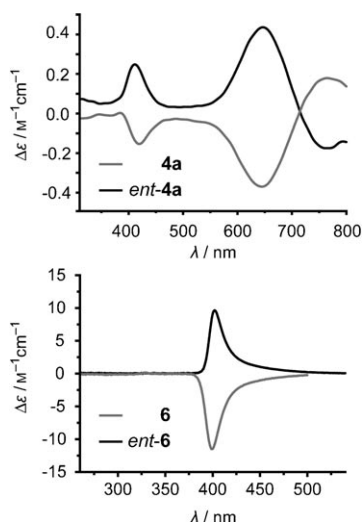
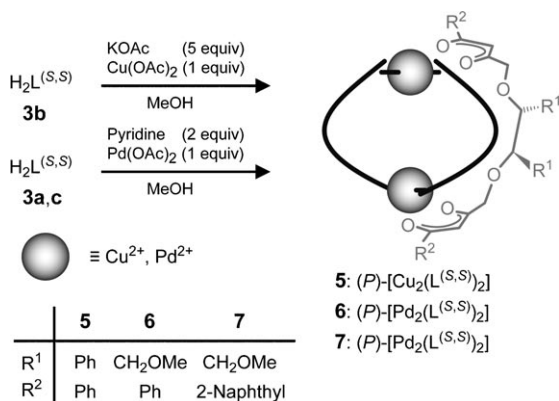


Figure 2. Top: CD spectrum of copper(II) cubanes (*C,C,C,C*)-[Cu₄(L^(S,S))₂-(OMe)₄] (**4a**) and (*A,A,A,A*)-[Cu₄(L^(R,R))₂(OMe)₄] (*ent*-**4a**) (dichloromethane, 25 °C, *c* = 2.2 · 10⁻³ mol l⁻¹). Bottom: CD spectrum of palladium(II) helicates (*P*)-[Pd₂(L^(S,S))₂] (**6**) and (*M*)-[Pd₂(L^(R,R))₂] (*ent*-**6**) (dichloromethane, 25 °C, **6**: *c* = 6.4 · 10⁻⁴ mol l⁻¹ and *ent*-**6**: *c* = 1.0 · 10⁻³ mol l⁻¹).

(L^(S,S))₂] (**5**) (Scheme 3). This was established by X-ray structure analysis on crystals, obtained by vapour diffusion of diethyl ether into a solution of (*P*)-[Cu₂(L^(S,S))₂] (**5**) in methanol/acetone (1:1).



Scheme 3. Synthesis and schematic presentation of (*P*)-[Cu₂(L^(S,S))₂] (**5**), (*P*)-[Pd₂(L^(S,S))₂] (**6**), and (*P*)-[Pd₂(L^(S,S))₂] (**7**), starting from H₂L^(S,S) (**3a-c**).

According to these analyses,^[17,18] double-stranded copper(II) helicate^[9,19] **5** crystallizes in the chiral monoclinic space group *C*2. Each copper ion has approximate square-planar coordination, formed by the chelating 1,3-diketo units of the ligands. Two phenyl substituents, each, of the parallel coordination spheres at copper (torsion angle 37°), are arranged in *trans*-positions, and the stereogenic centers of ligand (L^(S,S))₂²⁻ (**3b**)²⁻ induce *P*-helicity, resulting in an overall *D*₂ molecule symmetry of helicate **5** (Table 1, Figure 3). The Cu²⁺-Cu²⁺ distances (*d*_{intra} = *d*_{inter} = 3.55 Å) in **5** are rather short, indicating that the Cu²⁺-Cu²⁺ interaction

may involve nonbonding stacking of two d_{x²-y²} orbitals.^[20] The decisive role of the Cs⁺ and K⁺ ions for the formation

Table 1. Selected bond lengths [Å] and angles [°] for complexes **5–7**.

	5	6 ^[a]	7
<i>d</i> _{av} (M ²⁺ -O)	1.90	1.98 (1.99)	1.99
<i>d</i> _{intra} (M ²⁺ -M ²⁺)	3.55	3.27 (3.23)	3.26
<i>d</i> _{inter} (M ²⁺ -M ²⁺)	3.55	3.19 (3.23)	3.32
<i>d</i> _{inter aryl}	7.10	6.46 (6.46)	6.53
angle (M ²⁺ -M ²⁺ -M ²⁺)	176.5	180.0 (180.0)	165.9
torsion angle ^[b]	36.9	45.4 (39.9)	44.9
angle ^[c] M ²⁺	9.9	2.6 (3.9)	0.2

[a] Values for the disordered independent molecule in the unit cell (in brackets). [b] Torsion angle of the nearly parallel coordination spheres (averaged over the coordinating atoms). [c] Average angle, in which the chelating planes at one metal center are twisted to each other.

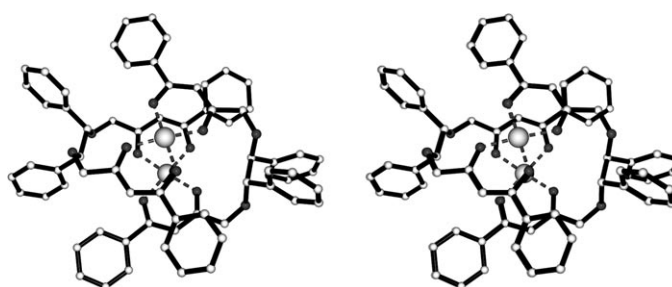


Figure 3. Stereoview of helicate (*P*)-[Cu₂(L^(S,S))₂] (**5**). C white, O dark grey, Cu grey; hydrogen atoms omitted for clarity.

of the cubanes **4** and helicate **5** is still in the dark. However, in the absence of alkali ions, only polymeric material is isolated, insoluble in standard solvents.^[21]

The square-planar environment of the copper centers in **5** indicated that, in principle, it should be possible to generate this type of complex with second- and third-row d⁸-transition metals too. Due to their electronic structure, these complexes are diamagnetic and should enable the study of bulk properties with NMR spectroscopy. Indeed, reaction of one equivalent of H₂L^(S,S) (**3a,c**) and one equivalent of palladium(II) acetate in the presence of two equivalents of pyridine^[22] afforded the palladium(II) helicates (*P*)-[Pd₂(L^(S,S))₂] (**6**) and (*P*)-[Pd₂(L^(S,S))₂] (**7**) in 92 and 95 % yield, respectively (Scheme 3). ¹H NMR spectroscopy of double-stranded palladium(II) helicates^[20c,23] **6** and **7** displayed only one set of signals and variable-temperature experiments in [D₆]acetone and [D₅]bromobenzene did not show any dynamic effects in these systems.^[24] Final proof of the helical structure and the *trans-anti* arrangement of the substituents in (*P*)-[Pd₂(L^(S,S))₂] (**6**) and (*P*)-[Pd₂(L^(S,S))₂] (**7**) was achieved by X-ray structure analyses on single crystals obtained from solutions of the compounds on prolonged standing in [D₆]acetone and [D₅]bromobenzene, respectively.^[17,18] Helicates **5–7** are principally isostructural (Figure 3) and the slight differences in bond lengths and angles of **5–7** are summarized in Table 1. Solution-CD experiments of palladium(II) helicates **6** and *ent*-**6** (synthesized from H₂L^(R,R) (*ent*-

3a)^[8] in dichloromethane displayed a perfect mirror image with an slightly bathochromic-shifted, enhanced absorption at $\lambda_{\max} = 401$ nm, compared to the free ligand ($\lambda_{\max} = 367$ nm, not shown), which is induced by the helicity of complexes (*P*)-[Pd₂(L^(S,S))₂] (**6**) and (*M*)-[Pd₂(L^(R,R))₂] (*ent*-**6**) (Figure 2, bottom).^[25]

Most interesting, in the solid-state helicates **5–7** self-organize into polymeric superstructures with linear threading of the transition-metal ions, as exemplarily presented for (*P*)-[Pd₂(L^(S,S))₂]_∞ (**7**_∞; Figure 4).^[20d,f,26] The overlapping van der Waals radii of the palladium ions emphasize the close contacts of the metal ions. The intercomplex Cu–Cu or Pd–Pd van der Waals distances (d_{inter}) amount to 3.55 (**5**_∞), 3.19 (**6**_∞), and 3.32 Å (**7**_∞). The intercomplex aryl–aryl distances between individual cylinders are $d_{\text{inter}} = 7.10$, 6.46 and 6.53 Å for **5**_∞–**7**_∞, respectively. In any case, no close π – π contacts between the phenyl or naphthyl substituents in **5**_∞–**7**_∞ were observed. Stacking of planar transition complexes

through d–d orbital interactions between the metal centers into wirelike linear superstructures promises unique electroconductive, magnetic, and optical properties.^[20,26] In the cases of **6**_∞ and **7**_∞, the Pd²⁺–Pd²⁺ distances (Table 1) are of length similar to the interatomic distances in metallic palladium (2.74 Å),^[27] but longer than the double effective ionic radius of Pd²⁺ (1.72 Å)^[27] and close to the double van der Waals radius of palladium (3.26 Å).^[28] These data suggest substantial d⁸–d⁸ Pd²⁺–Pd²⁺ interactions.^[20]

In spite of oxygen donors present in the ligand backbone, no encapsulation of alkali ions in helicates **5–7** was observed, not even in solution.^[10] To make accessible chiral metallacoronates, we chose to put additional stress on the system by varying the preferential coordination geometry at the transition-metal center. Instead of penta- or tetracoordinate copper(II) or palladium(II), we introduced hexacoordinate nickel(II). Therefore, when H₂L^(S,S) (**3a**) was treated with lithium hydroxide monohydrate and nickel(II) acetate

tetrahydrate in methanol at room temperature, we isolated neutral heterochiral (dilithium)–dinickel(II) coronate [(Li·MeOH)₂·{(Δ,Λ)-Ni₂(L^(S,S))₂(OMe)₂}] (**8**) (Scheme 4).

Crystals, obtained by vapour diffusion of diethyl ether into a solution of **8** in methanol were subjected to an X-ray structure analysis (Table 1).^[17,18] According to this analysis, **8** crystallizes in the chiral orthorhombic space group *P*2₁2₁2 and possesses a dinuclear nickel(II) coronate framework,^[13b,29] composed of two ligands (L^(S,S))²⁻ (**3a**)²⁻ and two nickel ions. Each nickel ion has approximate octahedral coordination, consisting of two μ_1 -O donors and two μ_2 -O donors from each ligand and two μ_2 -(OMe)⁻ donors. Ni(1) has Λ - and Ni(2) has Δ -configuration ($d_{\text{Ni-Ni}} = 3.08$ Å).^[15] However, because of the stereogenic centers of (L^(S,S))²⁻, **8** is not a mesocate,^[30] but rather exists as a single enantiomer with idealized C₂ molecule symmetry (C₂ axis running through the two nickel(II) centers). The two halves of the nickel(II) coronate backbone, each host a lithium cation ($d_{\text{Li-Li}} = 6.14$ Å) with approximate

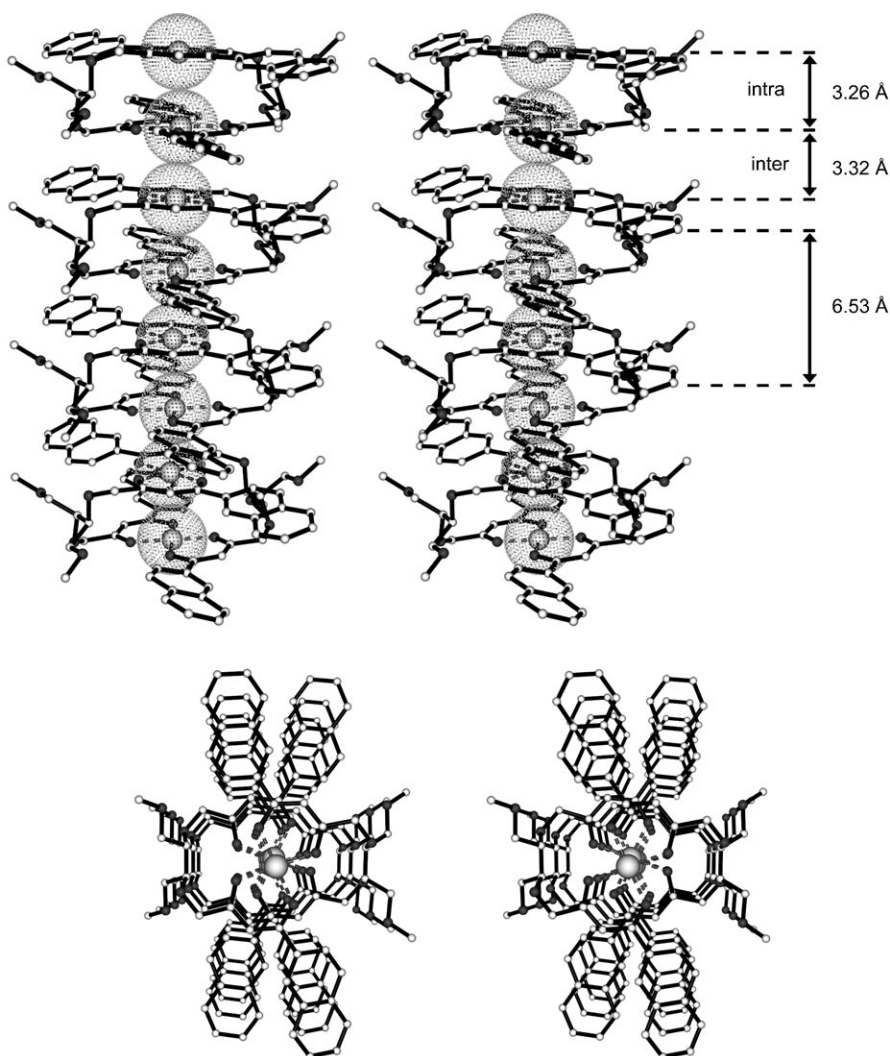
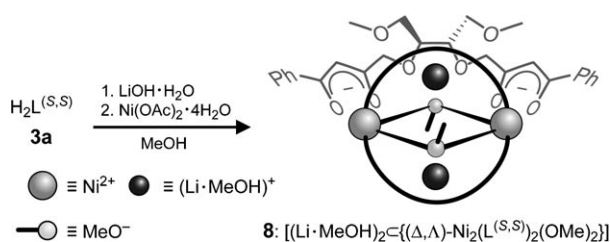


Figure 4. Top: Stereoview of wire-like superstructure of helicate (*P*)-[Pd₂(L^(S,S))₂]_n (**7**_n) ($n=4$, side view), exhibiting an linear overlap of the palladium d₂ orbitals. Bottom: Stereoview of **7**_n ($n=3$, top view along the *b* axis) of one independent molecule in the unit cell. C white, O grey, Pd light grey, van der Waals radii of Pd light grey (dotted); hydrogen atoms omitted for clarity.



Scheme 4. Synthesis and schematic presentation of $[(\text{Li}\cdot\text{MeOH})_2\text{C}\{(\Delta,\Lambda)\text{-Ni}_2(\text{L}^{(S,S)})_2(\text{OMe})_2\}]$ (**8**), starting from $\text{H}_2\text{L}^{(S,S)}$ (**3a**).

square-pyramidal coordination of two carbonyl μ_2 -O donors and two ether μ_2 -O donors of one ligand ($\text{L}^{(S,S)})^{2-}$ and a μ_1 -O donor of methanol (Figure 5).

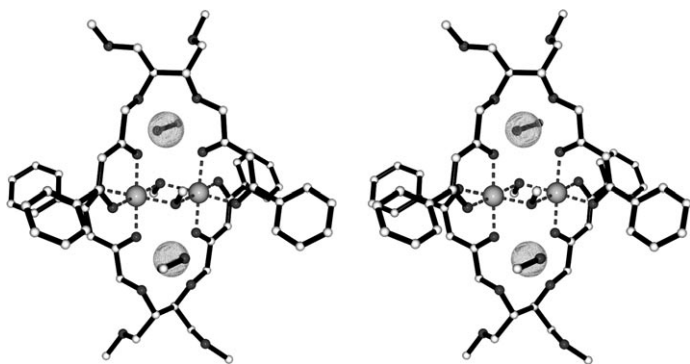


Figure 5. Stereoview of (dilithium)-dinickel(II) coronate $[(\text{Li}\cdot\text{MeOH})_2\text{C}\{(\Delta,\Lambda)\text{-Ni}_2(\text{L}^{(S,S)})_2(\text{OMe})_2\}]$ (**8**), disorder and hydrogen atoms are omitted for clarity. C white, O dark grey, Ni grey, Li light grey (dotted).

Conclusion

Starting from enantiomerically pure ligands $\text{H}_2\text{L}^{(S,S)}$ (**3**), we present in this contribution the efficient synthesis of three different types of polynuclear complexes **4–8** through diastereoselective self-organization. The nuclearity and the coordination geometry at the transition-metal centers of the chiral cubic, helical, and metallacoronate systems **4–8** were controlled by the appropriate choice and ratio of transition-metal ion, alkali-metal ion, and ligand. Furthermore, helicates **5–7** undergo polyassociation in the solid state to generate polymeric architectures containing linear arrays of copper(II) and palladium(II) ions. The structures of complexes **4–8** were solved by the combination of mass spectrometry, NMR spectroscopy, and single-crystal X-ray analyses. The diastereoselectivity of the self-organization was demonstrated by circular dichroism measurements of the enantiomers for complexes **4a** and **6**. Due to their optical purity and their arrangement in the solid state, complexes **4–8** could function as model systems for magnetochiral or electroconductive studies.

Experimental Section

General techniques: Unless stated otherwise, all manipulations were carried out under dry dinitrogen atmosphere and the solvents used were purified and dried according to standard procedures. All reagents employed (high-grade purity materials) were commercially available and used as supplied (Fluka, Aldrich, and Acros Organics). The enantiomerically pure diols (2*S*,3*S*)-1,4-dimethoxy-2,3-butanediol (**1a**; 38715)^[31] and its enantiomer *ent*-**1a** (38710) are available from Fluka, (*S,S*)-(-)-hydrobenzoin (**1b**; 256269) from Aldrich. Flash chromatography was carried out using silica gel 60 Å (230–400 mesh, Merck grade 9385). For thin-layer chromatography (TLC), Merck silica gel 60 Å (layer: 0.20 mm) with fluorescent indicator UV₂₅₄ on aluminium sheets (5 × 10 cm) was used. Melting points were determined on a WAGNER-MUNZ apparatus and are not corrected. IR spectra were recorded as films or powder films on a ASI React IR-1000 spectrometer. NMR spectra were obtained from dilute solutions in CDCl₃ at approximately 25 °C, unless stated otherwise, and recorded on a JEOL EX400 spectrometer (¹H 400.1 MHz, ¹³C 100.5 MHz). The residual solvent signals were used as internal standards: CDCl₃ (¹H δ = 7.27 ppm, ¹³C δ = 77.0 ppm), [D₆]acetone (¹H δ = 2.05 ppm; ¹³C δ = 29.85 ppm), and [D₅]bromobenzene (¹H δ = 7.17 ppm, ¹³C δ = 122.51 ppm).^[32] The resonance multiplicity is indicated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). In solution ligands $\text{H}_2\text{L}^{(S,S)}$ (**3**) are present as a tautomeric mixture of the diketo, mono-enol, and bisenol species. Below, only signals of the dominating bisenol form are listed. FAB-MS spectra were recorded on a Micromass ZAB-Spec (Cs⁺) spectrometer with *m*-NBA as matrix. Circular dichroism (CD) measurements were carried out on a JASCO J 710 spectropolarimeter (Xe-lamp) with optical grade solvents and quartz glass cuvettes with a 5 mm path length. Optical rotations were measured on a Perkin Elmer 341 polarimeter. Elemental analyses were performed on a Carlo Erba EA1110 CHN instrument and on a HERAEUS CHN-Mikroautomat.

Single-crystal X-ray structure analyses: Details of crystal data, data collection and refinement are given in Table 2. X-ray data for **4b**, and **5'**^[33] were collected on a Nonius Kappa CCD area detector, with MoK α radiation (λ = 0.71073 Å). The structures were solved by direct methods with SHELXS-97^[34] and refined with full-matrix least-squares against F^2 with the SHELXL-97 program system.^[35] Lorentz, polarization, and absorption corrections^[36] were applied. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were fixed in ideal positions (riding model) and were included without refinement and with fixed isotropic U . In case of **4b**, C31–C34 of the aromatic ring are disordered with a ratio of 65:35%. The occupation of the cocrystallizing CHCl₃ molecule was set to 50%, the carbon C100 of the solvate molecule was refined only isotropically. In case of **5'**, carbon atoms of the phenyl substituent (C11–C16) showed disorder with an occupation of 51:49.

Data for **5–8** were collected on a Bruker-Nonius Kappa CCD diffractometer with MoK α radiation (λ = 0.71073 Å), and a graphite monochromator. The structures were solved by direct methods, and full-matrix least-squares refinements were carried out on F^2 by using SHELXTL NT6.12.^[37] A semi-empirical absorption correction based on multiple scans (SADABS)^[38] was performed. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically positioned with isotropic displacement parameters being either 1.2 U_{eq} or 1.5 U_{eq} of the preceding C atom. Disorder was found in structures **6** and **8**. A number of restraints (SIMU and DFIX, respectively) were applied in the treatment of this disorder. In the case of **6**, one of the two independent molecules showed disorder on the CH₃OCH₂ moiety with a refined occupation of the two preferred orientations of 52.8(5) and 47.2(5)%. In **8**, oxygen O3 was subjected to positional disorder with occupations of the two refined sites of 67(2)% for O3 and 33(2)% for O3'. In addition, there was a disordered methanol solvate molecule located on a crystallographic twofold rotation axis; no hydrogen atoms were included for this in the structure model.

(2*S*,3*S*)-1,4-Dimethoxy-(2,3-ethylacetoxy)-butane [(*S,S*)-2a**]:** A solution of (2*S*,3*S*)-1,4-dimethoxy-2,3-butanediol (*S,S*)-**1a** (4.00 g, 26.60 mmol) in dry THF (100 mL) was added dropwise to a suspension of sodium hy-

Table 2. Crystal and structure refinement data for complexes **4b**, **5**–**8**.

	4b	5	5 ^[33]	6	7	8
formula	C ₇₂ H ₆₈ Cu ₄ O ₁₆ ·CHCl ₃	C ₆₈ H ₅₆ Cu ₂ O ₁₂	C ₆₈ H ₅₆ Cu ₂ O ₁₂	C ₅₂ H ₅₆ O ₁₆ Pd ₂	C ₆₈ H ₆₄ O ₁₆ Pd ₂	C ₅₆ H ₇₀ Li ₂ Ni ₂ O ₂₀ ·0.5 CH ₃ OH
<i>M</i> _r [g mol ⁻¹]	1562.88	1192.21	1192.21	1149.77	1349.99	1210.44
crystal size [mm ³]	0.20 × 0.20 × 0.15	0.14 × 0.12 × 0.09	0.15 × 0.10 × 0.10	0.08 × 0.07 × 0.05	0.32 × 0.18 × 0.11	0.24 × 0.12 × 0.10
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	<i>C</i> 2	<i>C</i> 2	<i>I</i> 222	<i>C</i> 2	<i>P</i> 2 ₁ 2 ₁ 2	<i>P</i> 2 ₁ 2 ₁ 2
<i>a</i> [Å]	28.1231(8)	30.791(3)	7.0923(5)	29.222(2)	29.890(3)	25.555(3)
<i>b</i> [Å]	6.9100(2)	7.0987(2)	14.0724(6)	6.4592(3)	6.5297(4)	25.569(3)
<i>c</i> [Å]	21.2674(7)	27.586(2)	27.4167(18)	28.950(3)	14.637(2)	8.8061(7)
β [°]	114.794(2)	116.588(5)	90	119.578(5)	90	90
<i>V</i> [Å ³]	3751.9(2)	5392.0(7)	2736.3(3)	4752.3(7)	2856.7(5)	5754.0(11)
<i>Z</i>	2	4	2	4	2	4
ρ _{calcd} [Mg m ⁻³]	1.383	1.469	1.447	1.607	1.569	1.397
<i>T</i> [K]	173(2)	100(2)	173(2)	100(2)	100(2)	100(2)
μ [mm ⁻¹]	1.288	0.858	0.845	0.831	0.704	0.730
<i>F</i> (000)	1606	2472	1236	2352	1384	2548
θ range [°]	2.25 to 27.49	3.30 to 27.00	2.66 to 25.00	3.45 to 27.10	3.40 to 27.87	3.56 to 26.37
index ranges	−35 ≤ <i>h</i> ≤ 36	−39 ≤ <i>h</i> ≤ 39	−8 ≤ <i>h</i> ≤ 8	−37 ≤ <i>h</i> ≤ 37	−39 ≤ <i>h</i> ≤ 39	−31 ≤ <i>h</i> ≤ 31
	−8 ≤ <i>k</i> ≤ 8	−9 ≤ <i>k</i> ≤ 9	−16 ≤ <i>k</i> ≤ 16	−8 ≤ <i>k</i> ≤ 8	−8 ≤ <i>k</i> ≤ 8	−31 ≤ <i>k</i> ≤ 31
	−27 ≤ <i>l</i> ≤ 27	−35 ≤ <i>l</i> ≤ 35	−32 ≤ <i>l</i> ≤ 32	−37 ≤ <i>h</i> ≤ 37	−19 ≤ <i>l</i> ≤ 18	−10 ≤ <i>l</i> ≤ 10
reflns collected	8483	47 337	2433	42 701	26 852	52 678
independent reflns	8483	11 704	2433	10 473	6762	11 164
reflns observed [<i>I</i> > 2σ(<i>I</i>)]	7106	8341	1978	7250	6058	9790
max/min transmission	0.8303/0.7828	0.926/0.823	0.9202/0.8837	0.874/0.959	0.930/0.764	0.930/0.772
[<i>R</i> _{int}]	0.0000	0.0580	0.0000	0.0666	0.0346	0.0372
data/parameters	8483/459	11 704/739	2433/202	10 473/661	6762/390	11 164/751
goodness-of-fit on <i>F</i> ²	1.020	1.013	1.014	0.984	1.047	1.134
flack parameter ^[39]	0.09(2)	0.03(2)	−0.05(3)	0.03(3)	−0.01(2)	0.05(2)
final <i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0596	0.0654	0.0431	0.0375	0.0260	0.0501
<i>wR</i> 2 (all data)	0.1720	0.1767	0.1220	0.0757	0.0550	0.1159
largest residuals [e Å ⁻³]	1.305/−0.613	1.144/−0.545	0.413/−0.406	0.439/−0.423	0.385/−0.682	1.182/−0.540

drude (1.55 g, 59.00 mmol, 95%) in THF (100 mL), placed in a three-necked, round-bottomed flask (500 mL) equipped with a dropping funnel, a reflux condenser, and a nitrogen inlet. The suspension was stirred for further 30 min at room temperature and then a solution of ethyl bromoacetate (6.5 mL, 58.60 mmol) in THF (100 mL) was added slowly. After stirring overnight and reflux for 1 h, the reaction mixture was cautiously hydrolyzed by addition of distilled water (5 mL). The organic phase was removed (rotary evaporator, 40°C) and the residue was diluted with distilled water (20 mL). The aqueous phase was extracted with *n*-pentane (3 × 50 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated. The crude reaction product was purified by vacuum distillation. Yield: 3.77 g (44%), colorless oil; b.p. 210–220°C (≤ 5.0·10⁻⁴ mbar); [α]_D²⁵ = +8.1, [α]_D²⁵ = +8.4, [α]_D²⁵ = +9.4, [α]_D²⁵ = +17.2, [α]_D²⁵ = +35.6 (*c* = 0.01 in CHCl₃); ¹H NMR: δ = 4.28 (d, *J* = 16.8 Hz, 2H; O-CH_AH_B-CO), 4.26 (d, *J* = 16.8 Hz, 2H; O-CH_AH_B-CO), 4.15 (q, *J* = 7.2 Hz, 4H; CH₂-CH₃), 3.77–3.72 (m, 2H; O-CH), ¹⁴⁰ 3.68 (pseudo dd, *J* = 10.2, 3.0 Hz, 2H; CH-CH₂), ¹⁴⁰ 3.53 (pseudo dd, *J* = 10.2, 5.8 Hz, 2H; CH-CH₂), ¹⁴⁰ 3.31 (s, 6H; O-CH₃), 1.23 ppm (t, *J* = 7.2 Hz, 6H; CH₂-CH₃); ¹³C NMR: ¹⁴¹ δ = 170.70 (C=O), 79.78 (O-CH), 72.82 (CH-CH₂), 68.58 (O-CH₂-C=O), 60.59 (CH₂-CH₃), 59.03 (O-CH₃), 14.13 ppm (CH₂-CH₃); IR (film): $\tilde{\nu}$ = 2988, 2930, 2837, 1733, 1451, 1374, 1351, 1200, 1108, 1023, 870 cm⁻¹; MS: *m/z* (%): 323 (71) [M+H]⁺, 291 (67) [M-OCH₃]⁺, 277 (32) [M-OEt]⁺, 249 (21) [M-CO₂Et]⁺, 161 (43) [M/2]⁺, 115 (100) [M/2-OEt]⁺; (*ent*-**2a**): Prepared in analogy to **2a**, starting from *D*-tartaric acid: [α]_D²⁵ = −8.0, [α]_D²⁵ = −8.1, [α]_D²⁵ = −9.3, [α]_D²⁵ = −17.1, [α]_D²⁵ = −35.5 (*c* = 0.01 in CHCl₃); elemental analysis calcd (%) for C₁₄H₂₆O₈·0.5 H₂O (331.36): C 50.75, H 8.21; found: C 51.04, H 7.81.

(1*S*,2*S*)-1,2-Diphenyl-(1,2-ethylacetoxy)-ethane [(*S,S*)-2b**]**: Boron trifluoride diethyl etherate (0.47 mL, 3.81 mmol) was added dropwise to a cooled solution (0°C) of (*S,S*)-(-)-1,2-diphenyl-1,2-ethanediol (*S,S*)-**1b** (10.00 g, 46.60 mmol) and ethyl diazoacetate (11.7 mL, 93.20 mmol, ≤ 10% dichloromethane) in dichloromethane (100 mL), placed in a three-necked, round-bottomed flask (250 mL) equipped with a dropping

funnel, a reflux condenser, and a nitrogen inlet. The reaction mixture was stirred at room temperature for 1 h and then refluxed. After no progress of the reaction could be monitored by TLC (approx. 2 h), the solvents were removed with a rotary evaporator. The crude reaction product (yellowish oil) was further purified by column chromatography on silica gel (*i*-hexane/ethyl acetate 80:20). Yield: 5.43 g (30%), colorless solid, *R*_f = 0.29 (*i*-hexane/ethyl acetate 80:20); m.p. 53–54°C; [α]_D²⁵ = +43.7, [α]_D²⁵ = +45.2, [α]_D²⁵ = +50.9, [α]_D²⁵ = +82.4, [α]_D²⁵ = +120.1 (*c* = 0.01 in CHCl₃); ¹H NMR: δ = 7.19–7.08 (m, 6H; Ar-CH_{meta,para}), 7.03–6.96 (m, 4H; Ar-CH_{ortho}), 4.72 (s, 2H; O-CH), 4.14 (d, *J* = 16.4 Hz, 2H; O-CH_AH_B), 4.14 (q, *J* = 7.2 Hz, 4H; CH₂-CH₃), 4.06 (d, *J* = 16.4 Hz, 2H; O-CH_AH_B), 1.21 ppm (t, *J* = 7.2 Hz, 6H; CH₂-CH₃); ¹³C NMR: ¹⁴¹ δ = 170.28 (C=O), 137.09 (Ar-C_{ipso}), 127.99 (4C, Ar-CH_{meta}), 127.83 (Ar-CH_{para}), 127.78 (4C, Ar-CH_{ortho}), 85.95 (CH), 66.86 (O-CH₂), 60.61 (O-CH₂-CH₃), 14.09 ppm (CH₂-CH₃); IR (film): $\tilde{\nu}$ = 2997, 2985, 2944, 2914, 1752, 1445, 1418, 1376, 1198, 1133, 1027, 961, 702 cm⁻¹; MS: *m/z* (%): 387 (12) [M+H]⁺, 283 (100) [M-OCH₂CO₂Et]⁺, 193 (93) [M/2]⁺, 179 (72) [M-(OCH₂CO₂Et)₂-H]⁺; elemental analysis calcd (%) for C₂₂H₂₆O₆·0.25 H₂O (390.95): C 67.59, H 6.83; found: C 67.51, H 6.85.

General procedure for the synthesis of H₂L^(*S,S*) (3**)**^[9,13]: A solution of methyl ketone (35.3 mmol) in THF (50 mL) was added dropwise to a stirred suspension of sodium amide (2.75 g, 70.4 mmol, 95%) in THF (50 mL) at room temperature. After 10 min the resulting mixture was treated with a solution of diester **2** (16.0 mmol) in THF (50 mL), which was added dropwise over 5 min. The mixture was refluxed for 4 h and after cooling the solution to room temperature, the solvent was removed. The residue was hydrolyzed with 1 M hydrochloric acid (100 mL) and extracted with ethyl acetate (3 × 100 mL). The combined extracts were washed with distilled water (2 × 100 mL), dried over anhydrous sodium sulfate, and filtered. Removal of the solvent afforded **3** as an oil which crystallized at low pressure (oil pump).

(2*S*,3*S*)-1,1'-Diphenyl-4,4'-(1,4-dimethoxy-2,3-butanedioxy)dibutane-1,3-dione [(*S,S*)-3a**]**: For the experimental data of H₂L^(*S,S*) [(*S,S*)-**2a**], see ref-

erence [8]. ¹H NMR ([D₅]bromobenzene): δ = 16.61 (brs, 2H; OH), 8.05 (dd, *J* = 8.5, 1.3 Hz, 4H; Ar-CH_{ortho}), 7.47–7.40 (m, 2H; Ar-CH_{para}), 7.40–7.33 (m, 4H; Ar-CH_{meta}), 6.91 (s, 2H; =CH), 4.58 (d, *J* = 16.7 Hz, 2H; O-CH_ACH_B), 4.53 (d, *J* = 16.7 Hz, 2H; O-CH_ACH_B), 4.06–3.99 (m, 2H; O-CH), ¹⁴⁰ 3.82 (pseudo dd, *J* = 10.4, 2.9 Hz, 2H; CH-CH₂), ¹⁴⁰ 3.74 (pseudo dd, *J* = 10.4, 6.0 Hz, 2H; CH-CH₂), ¹⁴⁰ 3.40 ppm (s, 6H; O-CH₃); ¹³C NMR ([D₅]bromobenzene): ¹⁴¹ δ = 194.93 (C=O), 183.10 (C-OH), 134.77 (Ar-C_{ipso}), 132.51 (Ar-CH_{para}), 128.72 (4C, Ar-CH_{meta}), 127.33 (4C, Ar-CH_{ortho}), 93.84 (=CH), 80.10 (O-CH), 72.78 (O-CH₂), 72.51 (CH-CH₂), 59.11 ppm (O-CH₃).

(1*S*,2*S*)-1,1'-Diphenyl-4,4'-(1,2-diphenyl-1,2-ethanedioxy)dibutane-1,3-dione [(*S,S*)-3b**]:** Diester (*S,S*)-**2b** (6.18 g), acetophenone (4.12 mL); yield: 1.80 g (21%), slightly pink-colored crystals from methanol, *R*_f = 0.29 (*i*-hexane/ethyl acetate 80:20); m.p. 108–109°C; [*α*]_D = +108.5, [*α*]₅₇₈²⁵ = +113.5, [*α*]₅₄₆²⁵ = +132.8, [*α*]₄₃₆²⁵ = +290.2 (*c* = 0.01 in CHCl₃); ¹H NMR: δ = 15.91 (brs, 2H; OH), 7.85–7.78 (m, 4H; Ar-CH_{ortho}), 7.53–7.45 (m, 2H; Ar-CH_{para}), 7.44–7.33 (m, 4H; Ar-CH_{meta}), 7.24–7.16 (m, 6H; CH-Ar-CH_{meta,para}), 7.12–7.03 (m, 4H; CH-Ar-CH_{ortho}), 6.81 (s, 2H; =CH), 4.71 (s, 2H; O-CH), 4.24 (d, *J* = 16.9 Hz, 2H; O-CH_AH_B), 4.09 ppm (d, *J* = 16.9 Hz, 2H; O-CH_AH_B); ¹³C NMR: ¹⁴¹ δ = 194.49 (C=O), 183.42 (C-OH), 136.97 (CH-Ar-C_{ipso}), 134.39 (Ar-C_{ipso}), 132.51 (Ar-CH_{para}), 128.53 (4C, Ar-CH_{ortho} or *meta*), 128.24 (4C, CH-Ar-CH_{ortho} or *meta*), 128.15 (CH-Ar-CH_{para}), 127.97 (4C, CH-Ar-CH_{ortho} or *meta*), 127.14 (4C, Ar-CH_{ortho} or *meta*), 93.70 (=CH), 86.44 (O-CH), 70.69 ppm (O-CH₂); *ν* = 3134, 3065, 3030, 2895, 2833, 1598, 1575, 1471, 1424, 1343, 1266, 1212, 1108, 1027, 695 cm⁻¹; MS: *m/z* (%): 536 (35) [*M*+H]⁺, 357 (100) [*M*-OCH₂COCH₂COPh]⁺, 267 (41) [*M*/2]⁺, 161 (43) [CH₂COCH₂COPh]⁺; elemental analysis calcd (%) for C₃₄H₃₀O₆ (534.61): C 76.39, H 5.66; found: C 76.10, H 5.78.

(2*S*,3*S*)-1,1'-Di-(2-naphthyl)-4,4'-(1,4-dimethoxy-2,3-butanedioxy)dibutane-1,3-dione [(*S,S*)-3c**]:** Diester (*S,S*)-**2a** (5.16 g), 2-acetonaphthone (6.01 g); yield: 0.548 g (6%), beige microcrystalline material from methanol, *R*_f = 0.47 (*i*-hexane/ethyl acetate 60:40); m.p. 83–84°C; [*α*]_D = +16.1, [*α*]₅₇₈²⁵ = +17.7, [*α*]₅₄₆²⁵ = +22.2, [*α*]₄₃₆²⁵ = +79.3 (*c* = 0.01 in CHCl₃); ¹H NMR: δ = 15.95 (brs, 2H; OH), 8.40 (s, 2H; Ar-C-H), 7.87 (d, *J* = 8.5 Hz, 2H; Ar-C-H), 7.86 (d, *J* = 8.8 Hz, 2H; Ar-C-H), 7.91–7.75 (m, 8H; Ar-C-H), 6.78 (s, 2H; =CH), 4.47 (d, *J* = 16.6 Hz, 2H; O-CH_AH_B), 4.38 (d, *J* = 16.6 Hz, 2H; O-CH_AH_B), 3.91–3.85 (m, 2H; O-CH), ¹⁴⁰ 3.74 (pseudo dd, *J* = 10.4, 2.8 Hz, 2H; CH-CH₂), ¹⁴⁰ 3.62 (pseudo dd, *J* = 10.4, 5.6 Hz, 2H; CH-CH₂), ¹⁴⁰ 3.41 ppm (s, 6H; O-CH₃); ¹³C NMR: ¹⁴¹ δ = 194.68 (C=O), 182.68 (C-OH), 135.25 (Ar-C_{ipso}), 132.63 (Ar-C), 131.60 (Ar-C), 129.28 (Ar-C-H), 128.35 (Ar-C-H), 128.09 (4C, Ar-C-H), 127.68 (Ar-C-H), 126.71 (Ar-C-H), 123.00 (Ar-C-H), 93.94 (=CH), 79.96 (O-CH), 72.74 (O-CH₂), 72.09 (CH-CH₂), 59.30 ppm (O-CH₃); IR: *ν* = 3058, 2892, 2848, 2819, 1602, 1590, 1567, 1453, 1387, 1328, 1273, 1227, 1111, 1048, 816 cm⁻¹; MS: *m/z* (%): 571 (31) [*M*+H]⁺, 211 (39) [CH₂COCH₂COC₁₀H₇]⁺, 197 (20) [COCH₂COC₁₀H₇]⁺, 155 (100) [COC₁₀H₇]⁺; elemental analysis calcd (%) for C₃₄H₃₄O₈ (570.64): C 71.56, H 6.01; found: C 71.39, H 6.08.

General procedure for synthesis of cubanes [Cu₄(L^{(*S,S*))₂(OMe)₄] (4**):}** A hot solution of copper(II) acetate monohydrate (80 mg, 0.40 mmol) in methanol (8 mL) was added dropwise to a refluxing solution of H₂L^(*S,S*) (**3**) (0.20 mmol) and cesium acetate (39 mg, 0.20 mmol) in methanol (4 mL) (for the synthesis of **4b** potassium acetate (39.3 mg; 0.40 mmol) was used instead of cesium acetate). The reaction mixture was allowed to cool to room temperature and stirred for 30 min. After removal of the solvent (rotary evaporator, 40°C), the deep green residue was treated repeatedly (6×) with methanol (12 mL), which was removed by evaporation. The crude reaction product was suspended in methanol (12 mL), and the turquoise powder was filtered off. After drying under vacuum (oil pump), the solid material was crystallized from the indicated solvent by layering with methanol.

(*C,C,C,C*)-[Cu₄(L^{(*S,S*))₂(OMe)₄] (4a**) and (*A,A,A,A*)-[Cu₄(L^{(*R,R*))₂(OMe)₄] (*ent*-**4a**):}}** For the experimental data of copper(II) cubanes **4a** and *ent*-**4a**, see reference [8].

(*C,C,C,C*)-[Cu₄(L^{(*S,S*))₂(OMe)₄] (4b**):}** Bis-1,3-diketone **3b** (107 mg); yield: 130 mg (90%), dark-green cuboids suitable for X-ray analysis from chloroform; m.p. > 210°C (decomp); IR: *ν* = 3061, 3034, 2918, 2899, 2810, 1594, 1563, 1521, 1486, 1451, 1413, 1343, 1282, 1193, 1119, 1089, 1027,

973, 845, 760, 703 cm⁻¹; MS: *m/z* (%): 1325 (23) [Cu₂L₂+Cs]⁺ (Cs⁺ from the matrix), 1255 (73) [Cu₃L₂]⁺, 1215 (23) [Cu₂L₂+Na]⁺ (Na⁺ from the matrix), 1193 (38) [Cu₂L₂]⁺, 721 (38) [Cu₃L]⁺, 659 (62) [Cu₂L]⁺, 597 (100) [CuL+H]⁺; elemental analysis calcd (%) for C₇₂H₆₈Cu₄O₁₆ (1443.50): C 59.91, H 4.75; found: C 60.15, H 4.55.

(*C,C,C,C*)-[Cu₄(L^{(*S,S*))₂(OMe)₄] (4c**):}** Bis-1,3-diketone **3c** (114 mg); yield: 124 mg (82%), green crystals from dichloromethane; m.p. > 199°C (decomp); IR: *ν* = 3026, 2921, 2860, 2811, 1586, 1567, 1519, 1445, 1414, 1356, 1339, 1291, 1285, 1200, 1179, 1133, 1106, 1077, 1038, 976, 863, 780, 758 cm⁻¹; MS: *m/z* (%): 1397 (13) [Cu₂L₂+Cs]⁺ (Cs⁺ from the matrix), 1327 (47) [Cu₃L₂]⁺, 1287 (33) [Cu₂L₂+Na]⁺ (Na⁺ from the matrix), 1265 (100) [Cu₂L₂+H]⁺, 759 (25) [Cu₃L]⁺, 695 (82) [Cu₂L]⁺, 633 (61) [CuL+H]⁺; elemental analysis calcd (%) for C₇₂H₇₆Cu₄O₂₀ (1515.56): C 57.06, H 5.05; found: C 56.85, H 4.92.

(*P*)-[Cu₂(L^{(*S,S*))₂] (5**):}** Tetraketone **3b** (54 mg, 0.10 mmol) was dissolved in boiling methanol (2 mL) in the presence of potassium acetate (49 mg, 0.50 mmol). After approximately 2 min, a solution of copper(II) acetate monohydrate (20 mg, 0.10 mmol) in methanol (2 mL) was added dropwise and the reaction mixture was stirred after cooling to room temperature for further 30 min. After filtration over celite and dilution of the mother liquor by addition of acetone (4 mL), green prisms suitable for X-ray structure analysis were obtained by vapor diffusion of diethyl ether. Yield: 57 mg (95%); m.p. > 235°C (decomp); IR: *ν* = 3069, 3034, 2922, 2891, 2833, 1594, 1563, 1513, 1486, 1455, 1420, 1378, 1336, 1258, 1173, 1131, 1089, 1027, 973, 842, 753, 703 cm⁻¹; MS: *m/z* (%): 1215 (100) [Cu₂L₂+Na]⁺ (Na⁺ from the matrix), 1193 (18) [Cu₂L₂+H]⁺, 681 (26); elemental analysis calcd (%) for C₆₈H₅₆Cu₂O₁₂·0.5 H₂O (1201.28): C 67.99, H 4.78; found: C 68.15; H 4.63.

General procedure for synthesis of helicates (*P*)-[Pd₂(L^{(*S,S*))₂] (6,7**):}** Tetraketone **3a** or **c** (0.05 mmol) was dissolved in boiling methanol (2 mL) in the presence of pyridine (16 μL, 0.20 mmol). After approximately 2 min, a solution of palladium(II) acetate (23 mg, 0.10 mmol) in methanol (2 mL) was added dropwise and the reaction mixture was stirred after cooling to room temperature for further 2 h. After concentration of the solvent (ca. 1 mL; rotary evaporator, 40°C) and filtration over celite, an orange microcrystalline material was obtained by vapor diffusion of diethyl ether.

(*P*)-[Pd₂(L^{(*S,S*))₂] (6**):}** Bis-1,3-diketone **3a** (24 mg); yield: 27 mg (92%); yellow prisms suitable for X-ray analysis from [D₆]acetone; m.p. > 220°C (decomp); ¹H NMR ([D₆]acetone): ¹²⁴ δ = 7.62–7.52 (m, 6H; Ar-CH_{ortho,para}), 7.41–7.33 (m, 4H; Ar-CH_{meta}), 5.27 (s, 2H; =CH), 4.38 (d, *J* = 17.6 Hz, 2H; O-CH_ACH_B), 4.36–4.31 (m, 2H; O-CH), ¹⁴⁰ 4.29 (d, *J* = 17.6 Hz, 2H; O-CH_ACH_B), 3.81 (d, *J* = 8.8 Hz, 2H; CH-CH_AH_B), ¹⁴⁰ 3.50–3.42 (m, 2H; CH-CH_AH_B, partially hidden by the singlet of OCH₃), ¹⁴⁰ 3.49 ppm (s, 6H; O-CH₃); ¹³C NMR ([D₆]acetone): ¹⁴¹ δ = 189.82 (Ar-C=O), 177.72 (C=O), 135.84 (Ar-C_{ipso}), 132.26 (Ar-CH_{para}), 128.80 (4C, Ar-CH_{ortho}), 128.76 (4C, Ar-CH_{meta}), 93.96 (=CH), 79.86 (O-CH), 74.88 (O-CH₂), 73.54 (CH-CH₂), 59.81 ppm (O-CH₃); ¹H NMR ([D₅]bromobenzene): ¹²⁴ δ = 7.80 (m, 4H; Ar-CH_{ortho}), 7.62–7.55 (m, 2H; Ar-CH_{para}), 7.50–7.44 (m, 4H; Ar-CH_{meta}, partially hidden by solvent residual peaks), 5.33 (s, 2H; =CH), 4.80 (d, *J* = 7.3 Hz, 2H; O-CH), ¹⁴⁰ 4.67 (d, *J* = 17.3 Hz, 2H; O-CH_ACH_B), 4.47 (d, *J* = 17.3 Hz, 2H; O-CH_ACH_B), 4.18 (d, *J* = 9.3 Hz, 2H; CH-CH₂), ¹⁴⁰ 3.77 (dd, *J* = 9.3, 7.3 Hz, 2H; CH-CH₂), ¹⁴⁰ 3.55 ppm (s, 6H; O-CH₃); ¹³C NMR ([D₅]bromobenzene): ¹⁴¹ δ = 188.65 (Ar-C=O), 177.15 (C=O), 135.38 (Ar-C_{ipso}), 128.39 (4C, Ar-CH_{ortho}), (Ar-CH_{para} hidden by solvent residual peaks), 127.97 (4C, Ar-CH_{meta}), 93.54 (=CH), 79.28 (O-CH), 74.55 (CH-CH₂), 73.20 (O-CH₂), 59.67 ppm (O-CH₃); IR: *ν* = 2980, 2903, 2810, 1590, 1567, 1513, 1486, 1455, 1417, 1336, 1274, 1204, 1274, 1204, 1139, 1112, 1081, 1031, 1000, 973, 953, 930, 865, 795, 753 cm⁻¹; MS: *m/z* (%): 1283 (2) [Pd₂L₂+Cs]⁺ (Cs⁺ from the matrix), 1255 (3) [Pd₃L₂]⁺, 1151 (100) [Pd₂L₂+H]⁺, 681 (14) [PdL]⁺, 575 (21) [PdL]⁺; elemental analysis calcd (%) for C₅₂H₅₆O₁₆Pd₂·0.5 H₂O (1158.81): C 53.90, H 4.96; found: C 53.96, H 4.98. Complex *ent*-**6** was prepared in analogy to **6** from H₂L^(*R,R*) (*ent*-**3a**).¹⁸

(*P*)-[Pd₂(L^{(*S,S*))₂] (7**):}** Bis-1,3-diketone **3c** (29 mg); yield: 32 mg (95%); yellow right parallelepipeds suitable for X-ray analysis from [D₅]bromobenzene; m.p. > 220°C (decomp); ¹H NMR ([D₅]bromobenzene): ¹²⁴ δ = 8.25 (dd, *J* = 8.7, 1.7 Hz, 2H; Ar-CH), 8.06 (d,

$J=8.7$ Hz, 2H; Ar-CH), 8.00 (d, $J=8.7$ Hz, 2H; Ar-CH), 7.85 (s, 2H; Ar-CH), 7.70–7.63 (m, 4H; Ar-CH), 7.62–7.55 (m, 4H; Ar-CH), 5.50 (s, 2H; =CH), 4.92 (d, $J=7.1$ Hz, 2H; O-CH)^[40] 4.78 (d, $J=17.2$ Hz, 2H; O-CH_ACH_B), 4.48 (d, $J=17.2$ Hz, 2H; O-CH_ACH_B), 4.30 (d, $J=9.2$ Hz, 2H; CH-CH₂)^[40] 3.96–3.89 (dd, $J=9.2$, 7.1 Hz, 2H; CH-CH₂)^[40] 3.68 ppm (s, 6H; O-CH₃); ¹³C NMR ([D₅]bromobenzene)^[41] $\delta=188.50$ (Ar-C=O), 177.34 (C=O), 135.01 (Ar-C_{ipso}), 133.12 (Ar-C_{ipso}), 132.55 (Ar-C_{ipso}), 131.80–122.20 (7 Ar-C-H-signals hidden by solvent residual peaks), 94.23 (=CH), 79.50 (O-CH), 74.44 (CH-CH₂), 73.19 (O-CH₂), 59.78 ppm (O-CH₃); IR: $\tilde{\nu}=3057$, 2976, 2926, 2845, 2810, 1567, 1505, 1436, 1417, 1328, 1270, 1200, 1135, 1104, 1069, 978, 950, 857, 772, 753 cm⁻¹; MS: m/z (%): 1351 (100) [Pd₂L₂+H]⁺; elemental analysis calcd (%) for C₆₈H₆₄O₁₆Pd₂·0.5 H₂O (1359.05): C 60.10, H 4.82; found: C 60.07, H 4.88.

[(Li·MeOH)₂C((Δ,Δ)-Ni₂(L^(S,S))₂(OMe)₂)] (8): Solid lithium hydroxide monohydrate (8 mg, 0.20 mmol) was added to a solution of tetraketone **3a** (48 mg, 0.1 mmol) in methanol (2 mL). After stirring for approximately 2 min, a solution of nickel(II) acetate tetrahydrate (16 mg, 0.066 mmol) in methanol (2 mL) was added dropwise and the reaction mixture was stirred for further 30 min at room temperature. After filtration of the turquoise solution over celite, green microcrystals were obtained by vapor diffusion of diethyl ether. Yield: 19 mg (48%); green right parallelepipeds suitable for X-ray analysis by recrystallization from methanol and vapor diffusion of diethyl ether. M.p. >210 °C (decomp); IR: $\tilde{\nu}=2988$, 2934, 2883, 2829, 1594, 1571, 1521, 1471, 1432, 1339, 1274, 1239, 1193, 1108, 1081, 1027, 977, 930, 853, 799, 764, 718, 695 cm⁻¹; MS: m/z (%): 1543 (10) [Ni₂L₃+Li]⁺, 1220 (27) [Ni₃L₂(OMe)₃+Li]⁺, 1128 (7) [Ni₂L₂(OMe)₂+Li]⁺, 1097 (10) [Ni₂L₂(OMe)+Li]⁺, 1059 (100) [Ni₂L₂+Li]⁺, 533 (38) [NiL+Li]⁺; elemental analysis calcd (%) for C₅₆H₇₀Li₂Ni₂O₂₀·0.5 H₂O (1203.47): C 55.89, H 5.95; found: C 55.69, H 5.86.

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- [1] a) E. Uller, B. Demleitner, I. Bernt, R. W. Saalfrank, *Struct. Bonding* **2000**, *96*, 149–175; b) R. Prakash, R. W. Saalfrank, H. Maid, A. Scheurer, F. W. Heinemann, A. X. Trautwein, L. H. Böttger, *Angew. Chem.* **2006**, *118*, 6017–6022; *Angew. Chem. Int. Ed.* **2006**, *45*, 5885–5889; c) M. D. Pluth, K. N. Raymond, *Chem. Soc. Rev.* **2007**, *36*, 161–171; d) D. K. Chand, K. Biradha, M. Kawano, S. Sakamoto, K. Yamaguchi, M. Fujita, *Chem. Asian J.* **2006**, *1–2*, 82–90; e) E. E. Moushi, T. C. Stamatatos, W. Wernsdorfer, V. Nastopoulos, G. Christou, A. J. Tasiopoulos, *Angew. Chem.* **2006**, *118*, 7886–7889; *Angew. Chem. Int. Ed.* **2006**, *45*, 7722–7725; f) E. S. Barrett, T. J. Dale, J. Rebek, Jr., *J. Am. Chem. Soc.* **2007**, *129*, 8818–8824; g) J. Heo, Y.-M. Jeon, C. A. Mirkin, *J. Am. Chem. Soc.* **2007**, *129*, 7712–7713; h) H.-B. Yang, A. M. Hawkrige, S. D. Huang, N. Das, S. D. Bunge, D. C. Muddiman, P. J. Stang, *J. Am. Chem. Soc.* **2007**, *129*, 2120–2129; i) R. M. McKinlay, J. L. Atwood, *Angew. Chem.* **2007**, *119*, 2446–2449; *Angew. Chem. Int. Ed.* **2007**, *46*, 2394–2397; j) E. G. Bardají, E. Freisinger, B. Costisella, C. A. Schalley, W. Brüning, M. Sabat, B. Lippert, *Chem. Eur. J.* **2007**, *13*, 6019–6039; k) M. Shanmugam, G. Chastanet, T. Mallah, R. Sessoli, S. J. Teat, G. A. Timco, R. E. P. Winpenny, *Chem. Eur. J.* **2006**, *12*, 8777–8785; l) C. M. Zaleski, J. W. Kampf, T. Mallah, M. L. Kirk, V. L. Pecoraro, *Inorg. Chem.* **2007**, *46*, 1954–1956; m) H. Oshio, M. Nihei, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 608–620; n) M. Albrecht, R. Fröhlich, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 797–808; o) C. Pariya, C. R. Sparrow, C.-K. Back, G. Sandí, F. R. Fronczek, A. W. Maverick, *Angew. Chem.* **2007**, *119*, 6421–6424; *Angew. Chem. Int. Ed.* **2007**, *46*, 6305–6308.
- [2] R. Breslow, *Artificial Enzymes*, Wiley-VCH, Weinheim, **2005**.
- [3] See: a) D. M. Vriezema, M. C. Aragonès, J. A. A. W. Elemans, J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, *Chem. Rev.* **2005**, *105*, 1445–1489; b) M. Yoshizawa, M. Tamura, M. Fujita, *Science* **2006**, *312*, 251–254; c) S. Polizu, O. Savadogo, P. Poulin, L.H. Yahia, *J. Nanosci. Nanotechnol.* **2006**, *6*, 1883–1904; d) F. C. Tucci, A. R. Renslo, D. M. Rudkevich, J. Rebek, Jr., *Angew. Chem.* **2000**, *112*, 1118–1121; *Angew. Chem. Int. Ed.* **2000**, *39*, 1076–1079.
- [4] cf.: a) C. H. Bennett, D. P. DiVincenzo, *Nature* **2000**, *404*, 247–255; b) M. N. Leuenerger, D. Loss, *Nature* **2001**, *410*, 789–793; c) W. A. Coish, D. Loss, arXiv: cond-mat 0606550 **2006**, 1–39; d) R. Prevedel, P. Walther, F. Tiefenbacher, P. Böhi, R. Kaltenbaek, T. Jennewein, A. Zeilinger, *Nature* **2007**, *445*, 65–69.
- [5] cf.: a) B. Barbara, L. Thomas, F. Lionti, I. Chiorescu, A. Sulpice, *J. Magn. Magn. Mater.* **1999**, *200*, 167–181; b) D. Gatteschi, R. Sessoli, A. Cornia, *Chem. Commun.* **2000**, 725–732; c) E. Coronado, J.-R. Galán-Mascarós, C.-J. Gómez-García, J. Ensling, P. Gütllich, *Chem. Eur. J.* **2000**, *6*, 552–563; d) R. Sessoli, D. Gatteschi, *Angew. Chem.* **2003**, *115*, 278–309; *Angew. Chem. Int. Ed.* **2003**, *42*, 268–297; e) L. M. Wittick, K. S. Murray, B. Moubarak, S. R. Batten, L. Spiccia, K. J. Berry, *Dalton Trans.* **2004**, 1003–1011; f) M. Murugesu, M. Habrych, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* **2004**, *126*, 4766–4767; g) M. Murugesu, W. Wernsdorfer, K. A. Abboud, G. Christou, *Angew. Chem.* **2005**, *117*, 914–918; *Angew. Chem. Int. Ed.* **2005**, *44*, 892–896; h) E. M. Rumberger, S. J. Shah, C. C. Beedle, L. N. Zakharov, A. L. Rheingold, D. N. Hendrickson, *Inorg. Chem.* **2005**, *44*, 2742–2752; i) R. W. Saalfrank, A. Scheurer, I. Bernt, F. W. Heinemann, A. V. Postnikov, V. Schünemann, A. X. Trautwein, M. S. Alam, H. Rupp, P. Müller, *Dalton Trans.* **2006**, 2865–2874; j) S. Accorsi, A.-L. Barra, A. Caneschi, G. Chastanet, A. Cornia, A. C. Fabretti, D. Gatteschi, C. Mortalò, E. Olivieri, P. Parenti, P. Rosa, R. Sessoli, L. Sorace, W. Wernsdorfer, L. Zobbi, *J. Am. Chem. Soc.* **2006**, *128*, 4742–4755; k) R. W. Saalfrank, A. Scheurer, R. Prakash, F. W. Heinemann, T. Nakajima, F. Hampel, R. Leppin, B. Pilawa, H. Rupp, P. Müller, *Inorg. Chem.* **2007**, *46*, 1586–1592; l) T. C. Stamatatos, K. A. Abboud, W. Wernsdorfer, G. Christou, *Angew. Chem.* **2007**, *119*, 902–906; *Angew. Chem. Int. Ed.* **2007**, *46*, 884–888.
- [6] See: a) H. Imai, K. Inoue, K. Kikuchi, Y. Yoshida, M. Ito, T. Sunahara, S. Onaka, *Angew. Chem.* **2004**, *116*, 5736–5739; *Angew. Chem. Int. Ed.* **2004**, *43*, 5618–5621; b) R. Andrés, M. Brissard, M. Gruselle, C. Train, J. Vaissermann, B. Malézieux, J.-P. Jamet, M. Verdager, *Inorg. Chem.* **2001**, *40*, 4633–4640; c) R. Andrés, B. Malézieux, M. Brissard, M. Gruselle, C. Train, M. Verdager, *Chirality* **2001**, *13*, 712–714; d) G. L. J. A. Rikken, E. Raupach, *Nature* **2000**, *405*, 932–935; e) G. L. J. A. Rikken, E. Raupach, *Nature* **1997**, *390*, 493–494.
- [7] J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**.
- [8] R. W. Saalfrank, C. Schmidt, H. Maid, F. Hampel, W. Bauer, A. Scheurer, *Angew. Chem.* **2006**, *118*, 322–325; *Angew. Chem. Int. Ed.* **2006**, *45*, 315–318.
- [9] R. W. Saalfrank, H. Maid, N. Mooren, F. Hampel, *Angew. Chem.* **2002**, *114*, 323–326; *Angew. Chem. Int. Ed.* **2002**, *41*, 304–307.
- [10] C. Spitzlei, Ph.D. Dissertation, Universität Erlangen-Nürnberg, **2006**.
- [11] For previous work based on L-tartaric acid derivatives, see: a) A. Scheurer, H. Maid, F. Hampel, R. W. Saalfrank, L. Toupet, P. Mosset, R. Puchta, N. J. R. van Eikema Hommes, *Eur. J. Org. Chem.* **2005**, 2566–2574; b) A. Scheurer, W. Bauer, F. Hampel, C. Schmidt, R. W. Saalfrank, P. Mosset, R. Puchta, N. J. R. van Eikema Hommes, *Tetrahedron: Asymmetry* **2004**, *15*, 867–872; c) R. Boulch, A. Scheurer, P. Mosset, R. W. Saalfrank, *Tetrahedron Lett.* **2000**, *41*, 1023–1026; d) A. Scheurer, P. Mosset, M. Spiegel, R. W. Saalfrank, *Tetrahedron* **1999**, *55*, 1063–1078; e) A. Scheurer, P. Mosset, R. W. Saalfrank, *Tetrahedron: Asymmetry* **1999**, *10*, 3559–3570; f) A. Scheurer, P. Mosset, R. W. Saalfrank, *Tetrahedron: Asymmetry* **1997**, *8*, 1243–1251 and 3161.

- [12] a) J. T. Adams, C. R. Hauser, *J. Am. Chem. Soc.* **1944**, *66*, 1220–1222; b) R. Levine, J. A. Conroy, J. T. Adams, C. R. Hauser, *J. Am. Chem. Soc.* **1945**, *67*, 1510–1512.
- [13] For other supramolecular structures based on tartaric acid-derived bis-1,3-diketo ligands, see: a) M. Albrecht, S. Dehn, R. Fröhlich, *Angew. Chem.* **2006**, *118*, 2858–2860; *Angew. Chem. Int. Ed.* **2006**, *45*, 2792–2794; b) M. Albrecht, S. Dehn, G. Raabe, R. Fröhlich, *Chem. Commun.* **2005**, 5690–5692; c) M. Albrecht, S. Schmid, M. deGroot, P. Weis, R. Fröhlich, *Chem. Commun.* **2003**, 2526–2527.
- [14] For the description of the chirality of **4**, see: a) A. von Zelewsky, *Stereochemistry of Coordination Compounds*, Wiley, Chichester, **1996**, p. 70; b) T. Damhus, C. E. Schäffer, *Inorg. Chem.* **1983**, *22*, 2406–2412; c) M. F. Brown, B. R. Cook, T. E. Sloan, *Inorg. Chem.* **1975**, *14*, 1273–1278.
- [15] For asymmetric induction via stereogenic centers during self-assembly, cf.: a) O. Mamula, A. von Zelewsky, P. Brodard, C.-W. Schläpfer, G. Bernardinelli, H. Stoeckli-Evans, *Chem. Eur. J.* **2005**, *11*, 3049–3057; b) H.-R. Tseng, S. A. Vignon, P. C. Celestre, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **2003**, *9*, 543–556; c) U. Knof, A. von Zelewsky, *Angew. Chem.* **1999**, *111*, 312–333; *Angew. Chem. Int. Ed.* **1999**, *38*, 302–322; d) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, *Chem. Eur. J.* **1999**, *5*, 1862–1873; e) E. J. Enemark, T. D. P. Stack, *Angew. Chem.* **1998**, *110*, 977–981; *Angew. Chem. Int. Ed.* **1998**, *37*, 932–935.
- [16] For recent literature on [Cu₄O₄] cores, see: a) C. Aronica, G. Chastanet, G. Pilet, B. Le Guennic, V. Robert, W. Wernsdorfer, D. Luneau, *Inorg. Chem.* **2007**, *46*, 6108–6119; b) M. Gottschaldt, R. Wegner, H. Görls, E.-G. Jäger, D. Klemm, *Eur. J. Inorg. Chem.* **2007**, 3633–3638; c) L. Xu, Y. Kim, S.-J. Kim, H. J. Kim, C. Kim, *Inorg. Chem. Commun.* **2007**, *10*, 586–589; d) V. T. Yilmaz, V. Kars, C. Kazak, *Z. Anorg. Allg. Chem.* **2007**, *633*, 351–353; e) B. Abarca, R. Ballesteros, M. Chadlaoui, C. Ramirez de Arellano, J. A. Real, *Eur. J. Inorg. Chem.* **2007**, 4574–4578; f) J. Fielden, J. Sprött, D.-L. Long, P. Kögerler, L. Cronin, *Inorg. Chem.* **2006**, *45*, 2886–2895; g) T. A. Hudson, K. J. Berry, B. Moubaraki, K. S. Murray, R. Robson, *Inorg. Chem.* **2006**, *45*, 3549–3556; h) Y.-M. Li, J.-J. Zhang, R.-B. Fu, S.-C. Xiang, T.-L. Sheng, D.-Q. Yuan, X.-H. Huang, X.-T. Wu, *Polyhedron* **2006**, *25*, 1618–1624; i) N. Lopez, T. E. Vos, A. M. Arif, W. W. Shum, J. C. Noveron, J. S. Miller, *Inorg. Chem.* **2006**, *45*, 4325–4327; j) J. Tercero, E. Ruiz, S. Alvarez, A. Rodríguez-Forteza, P. Alemany, *J. Mater. Chem.* **2006**, *16*, 2729–2735; k) A. Mukherjee, R. Raghunathan, M. K. Saha, M. Nethaji, S. Ramasesha, A. R. Chakravarty, *Chem. Eur. J.* **2005**, *11*, 3087–3096; l) J. K. Eberhardt, T. Glaser, R.-D. Hoffmann, R. Fröhlich, E.-U. Würthwein, *Eur. J. Inorg. Chem.* **2005**, 1175–1181; m) E. A. Buvaylo, V. N. Kokozay, O. Y. Vassilyeva, B. W. Skelton, J. Jezierska, L. C. Brunel, A. Ozarowski, *Inorg. Chem.* **2005**, *44*, 206–216.
- [17] For details of crystal data, data collection and refinement, *q. v.* Table 2 and general techniques.
- [18] CCDC 655727 (**4b**), CCDC 655728 (**5'**),^[33] and CCDC 656867–656870 (**5–8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic data centre via www.ccdc.cam.ac.uk/data_request/cif.
- [19] For double-stranded copper(II) helicates, cf.: a) T. K. Ronson, H. Adams, T. Riis-Johannessen, J. C. Jeffery, M. D. Ward, *New J. Chem.* **2006**, *30*, 26–28; b) A. R. Paital, P. K. Nanda, S. Das, G. Aromí, D. Ray, *Inorg. Chem.* **2006**, *45*, 505–507; c) M. Bera, G. Aromí, W. T. Wong, D. Ray, *Chem. Commun.* **2006**, 671–673; d) T. K. Ronson, H. Adams, M. D. Ward, *Inorg. Chim. Acta* **2005**, *358*, 1943–1954; e) C. J. Baylies, J. C. Jeffery, T. A. Miller, R. Moon, C. R. Rice, T. Riis-Johannessen, *Chem. Commun.* **2005**, 4158–4160; f) C. J. Sumby, P. J. Steel, *Inorg. Chem. Commun.* **2003**, *6*, 127–130; g) M. Vázquez, A. Taglietti, D. Gatteschi, L. Sorace, C. Sangregorio, A. M. González, M. Maneiro, R. M. Pedrido, M. R. Bermejo, *Chem. Commun.* **2003**, 1840–1841; h) M. R. Bermejo, R. Pedrido, A. M. González-Noya, M. J. Romero, M. Vázquez, L. Sorace, *New J. Chem.* **2003**, *27*, 1753–1759; i) T. Yano, R. Tanaka, T. Nishioka, I. Kinoshita, K. Isobe, L. J. Wright, T. J. Collins, *Chem. Commun.* **2002**, 1396–1397; j) P. E. Kruger, N. Martin, M. Nieuwenhuyzen, *J. Chem. Soc. Dalton Trans.* **2001**, 1966–1970; k) D. S. Marlin, M. M. Olmstead, P. K. Madscharak, *Inorg. Chim. Acta* **2001**, *323*, 1–4; l) C. R. Rice, S. Wörl, J. C. Jeffery, R. L. Paul, M. D. Ward, *Chem. Commun.* **2000**, 1529–1530.
- [20] For weak metal(II)–metal(II) d–d interactions, see: a) J. L. Pratihari, B. Shee, P. Pattanayak, D. Patra, A. Bhattacharyya, V. G. Puranik, C. H. Hung, S. Chattopadhyay, *Eur. J. Inorg. Chem.* **2007**, 4272–4281; b) M. Yoshizawa, K. Ono, K. Kumazawa, M. Fujita, *J. Am. Chem. Soc.* **2005**, *127*, 10800–10801; c) A. W. Maverick, R. K. Laxman, M. A. Hawkins, D. P. Martone, F. R. Fronczek, *Dalton Trans.* **2005**, 200–206; d) W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, C. Li, Z. Hui, *J. Am. Chem. Soc.* **2004**, *126*, 7639–7651; e) M. A. Haj, M. Quirós, J. M. Salas, J. A. Dobado, J. M. Molina, M. G. Basalote, M. Á. Máñez, *Eur. J. Inorg. Chem.* **2002**, 811–818; f) S.-W. Lai, T.-C. Cheung, M. C. W. Chan, K.-K. Cheung, S.-M. Peng, C.-M. Che, *Inorg. Chem.* **2000**, *39*, 255–262; g) X. S. Tan, Y. Fujii, R. Nukada, M. Mikuriya, Y. Nakano, *J. Chem. Soc. Dalton Trans.* **1999**, 2415–2416.
- [21] Surprisingly, in the synthesis of **4b** potassium acetate had to be used instead of cesium ions, otherwise a polymeric material was formed. In addition, the ratio of potassium and copper(II) acetate in the presence of H₂L^(5,5) (**3b**) determines the nuclearity of the supramolecular assemblies **4b** and **5**. For further examples of our group on the imperative use of alkaline ions in the formation of distinct supramolecular copper complexes, see also references [8–10, 26d].
- [22] Helicates **6** and **7** could also be generated in comparable yields in the presence of alkali metal acetates as bases. However, pyridine turned out to be more convenient since the co-crystallization and subsequent separation of the alkali metal acetates from **6** and **7** could be avoided.
- [23] For double-stranded palladium(II) helicates, see: a) H. J. Kitto, A. D. Rae, R. D. Webster, A. C. Willis, S. B. Wild, *Inorg. Chem.* **2007**, *46*, 8059–8070; b) H. Houjou, N. Schneider, Y. Nagawa, M. Kanetsato, R. Ruppert, K. Hiratani, *Eur. J. Inorg. Chem.* **2004**, 4216–4222; c) C. Mazet, L. H. Gade, *Inorg. Chem.* **2003**, *42*, 210–215; d) A. Orita, L. Jiang, T. Nakano, N. Ma, J. Otera, *Chem. Commun.* **2002**, 1362–1363; e) C. Mazet, L. H. Gade, *Chem. Eur. J.* **2002**, *8*, 4308–4318.
- [24] The helicates (P)-[Pd₂(L^(5,5))₂] (**6,7**) were sensitive to prolonged standing in deuterated chloroform probably due to traces of acidity (deposition of black solid materials), even when filtered over basic alumina.
- [25] H. Katagiri, Y. Tanaka, Y. Furusho, E. Yashima, *Angew. Chem.* **2007**, *119*, 2487–2491; *Angew. Chem. Int. Ed.* **2007**, *46*, 2435–2439.
- [26] a) A. M. Stadler, N. Kyritsakas, G. Vaughan, J.-M. Lehn, *Chem. Eur. J.* **2007**, *13*, 59–68; b) G. H. Clever, C. Kaul, T. Carell, *Angew. Chem.* **2007**, *119*, 6340–6350; *Angew. Chem. Int. Ed.* **2007**, *46*, 6226–6236; c) F.-A. Polonius, J. Müller, *Angew. Chem.* **2007**, *119*, 5698–5701; *Angew. Chem. Int. Ed.* **2007**, *46*, 5602–5604; d) R. A. Adrian, S. Zhu, D. R. Powell, G. A. Broker, E. R. T. Tiekinka, J. A. Walmsley, *Dalton Trans.* **2007**, 4399–4404; e) A. Hori, A. Shinohe, M. Yamasaki, E. Nishibori, S. Aoyagi, M. Sakata, *Angew. Chem.* **2007**, *119*, 7761–7764; *Angew. Chem. Int. Ed.* **2007**, *46*, 7617–7620; f) R. W. Saalfrank, A. Scheurer, R. Puchta, F. Hampel, H. Maid, F. W. Heinemann, *Angew. Chem.* **2007**, *119*, 269–272; *Angew. Chem. Int. Ed.* **2007**, *46*, 265–268; g) R. W. Saalfrank, N. Mooren, A. Scheurer, H. Maid, F. W. Heinemann, F. Hampel, W. Bauer, *Eur. J. Inorg. Chem.* **2007**, 4815–4822; h) B. H. Hong, S. C. Bae, C. W. Lee, S. Jeong, K. S. Kim, *Science* **2001**, *294*, 348–351; i) R. Palmans, D. B. MacQueen, C. G. Pierpont, A. J. Frank, *J. Am. Chem. Soc.* **1996**, *118*, 12647–12653.
- [27] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, **1990**.
- [28] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.
- [29] For nickel(II) coronates, see: a) G. Aromí, A. R. Bell, M. Helliwell, J. Raftery, S. J. Teat, G. A. Timco, O. Roubeau, R. E. P. Winpenny, *Chem. Eur. J.* **2003**, *9*, 3024–3032; b) G. Psomas, A. J. Stemmler, C. Dendrinou-Samara, J. J. Bodwin, M. Schneider, M. Alexiou, J. W.

- Kampf, D. P. Kessissoglou, V. L. Pecoraro, *Inorg. Chem.* **2001**, *40*, 1562–1570; c) S. T. Ochsenein, M. Murrie, E. Rusanov, H. Stoeckli-Evans, C. Sekine, H. U. Güdel, *Inorg. Chem.* **2002**, *41*, 5133–5140.
- [30] a) M. Albrecht, I. Janser, R. Fröhlich, *Chem. Commun.* **2005**, 157–165; b) D. L. Caulder, K. N. Raymond, *Angew. Chem.* **1999**, *111*, 3055–3058; *Angew. Chem. Int. Ed.* **1999**, *38*, 2878–2882; c) R. W. Saalfrank, V. Seitz, D. L. Caulder, K. N. Raymond, M. Teichert, D. Stalke, *Eur. J. Inorg. Chem.* **1998**, 1313–1317.
- [31] Diol **1a** was also generated by a four-step sequence from L-(+)-tartaric acid diethyl ester according to literature procedures: a) E. A. Mash, S. B. Hemperly, K. A. Nelson, P. C. Heidt, S. Van Deusen, *J. Org. Chem.* **1990**, *55*, 2045–2055; b) D. Seebach, H.-O. Kalinowski, B. Bastani, G. Crass, H. Daum, H. Dörr, N. P. DuPreez, V. Ehrig, W. Langer, C. Nüssler, H.-A. Oei, M. Schmidt, *Helv. Chim. Acta* **1977**, *60*, 301–325.
- [32] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512–7515.
- [33] If sodium acetate (0.50 mmol, 41.0 mg) was used instead of potassium acetate in the synthesis of **5** (otherwise identical reaction conditions),^[21] a green solid material could be isolated by filtration after stirring for further 30 min at room temperature. Dissolution of the precipitate was achieved in a mixture of methanol/acetone/dichloromethane (6 mL, 1:1:1) and further addition of pyrazine (0.50 mmol, 40.0 mg). After filtration over celite, green parallelepipeds of **5'** (yield: 52 mg; 87%), suitable for X-ray structure analysis, were obtained by vapor diffusion of diethyl ether.
- [34] G. M. Sheldrick, C. Krüger, P. Goddard, *Crystallographic Computing 3*, Oxford University Press, Oxford, **1985**, p. 175.
- [35] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, **1997**.
- [36] a) “Collect” data collection software, B. V. Nonius, **1998**; b) “Scale-pack” data processing software: Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326.
- [37] SHELXTL NT 6.12, Bruker AXS, Inc., Madison, WI, U. S. A., **2002**.
- [38] SADABS 2.06, Bruker AXS Inc., Madison, WI, USA, **2002**.
- [39] H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876–881.
- [40] The ¹H NMR spectra of the tartaric acid derived compounds **2a** and **3a,c** as well as complexes **6** and **7** are consistent with a symmetrical AA'BB'CC' six-spin system.^[8,11]
- [41] Due to the C₂ symmetry of compounds **2**, **3**, **6**, and **7**, each observed resonance in the ¹³C spectra originates from two carbon atoms, unless stated otherwise.

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