Coordination Polymers, 13[◇]

Induction of Helicity via Stereogenic Centers: Asymmetric Synthesis of (*P*)- and (*M*)-Coordination Polymers☆

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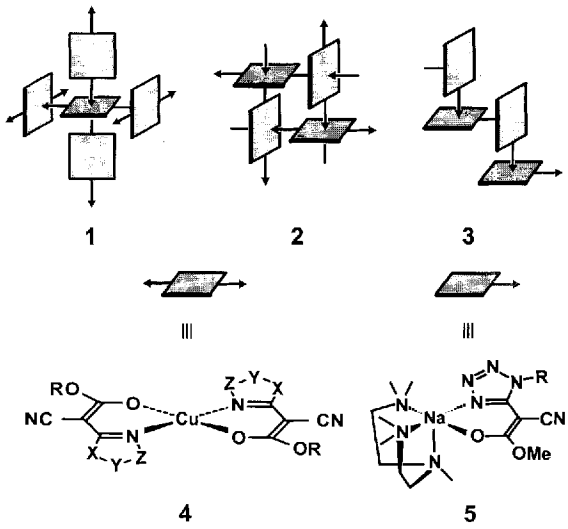
Reaction of a methanolic copper(II) acetate solution of enantiomerically pure (5*R*)-/(5*S*)-methyl *E*-(4-ethyl-2-oxazolidinylidene)cyanoacetate **6** leads to the mononuclear chelate complexes (*R*,*R*)-/(*S*,*S*)-**7**. Recrystallization of (*R*,*R*)-/(*S*,*S*)-**7** from non-coordinating chloroform and asymmetric induction via the stereogenic centers, originating from (*R*)-/(*S*)-**6**, stereospecifically yields the *right*- and *left*-handed helical 1D-coordination polymers (*P*)-/(*M*)-**8**. The structures of mononuclear complex (*R*,*R*)-**7** and of helix (*P*)-**8** and its mirror image (*M*)-**8** have been characterised unequivocally by X-ray crystal structure analyses. (*P*)- and (*M*)-**8** crystallize with chloroform to give the clathrates $^1_\infty\{[CuL^R_2] \cdot 2\ CHCl_3\}$ and $^1_\infty\{[CuL^S_2] \cdot 2\ CHCl_3\}$, respectively.

Most investigations of supramolecular helical complexes have focused on homopolynuclear racemic mixtures because of the achiral nature of the polynucleating ligands and the kinetic lability of the assemblies of the metals used[2]. Stereospecific triple[3–6] and double[7] dinuclear helices as well as double trinuclear helices[8] have been obtained either by the use of enantiomerically pure ligands[3,5,7] by spontaneous resolution during crystallization[4], or by chromatographic resolution[6,8].

Upon reaction of Cu^I and 2,6-bis[*N*-{2-(2-pyridyl)-ethyl}formimidoyl]-1-methoxybenzene], a single-stranded helical coordination polymer is formed. One of the two 1D-helices in the infinite unit cell is left-handed and the other right-handed[9]. To date, only a few examples of chiral, non-racemic helical coordination polymers have been reported[10,11], where the chirality is induced by a stereogenic center.

Our current research activities include the development of new strategies suitable for the generation of well-ordered aggregates, metallatopomers of coronates, and {2}/{3}-cryptates[12] as well as polymers. Recently we reported on the structures of 3D-$^3_\infty[CuL^1_2]$ **1**[13], 2D-$^2_\infty[CuL^2_2]$ **2**[14], and the 1D-coordination polymer $^1_\infty[NaL^3(PMDETA)]$ **3**[15]. A prerequisite for the generation of 3D-/2D-polymers **1** and **2** is the intermediate formation of the coordinatively unsaturated, bidentate copper(II) building blocks **4**. Reduced dimensionality was achieved by using a Group-11 metal. In



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the case of 1D-polymer **3**, only one cyano group per monomeric unit **5** is available for coordination to another metal center. A common feature of the three polymers is the distorted tetragonal-bipyramidal coordination of the metal centers.

In order to contribute additional material to the chemistry of the solid state, we applied our strategy for the development of coordination polymers **1**–**3** to ligand (*R*)-/(*S*)-**6**. In this paper we report on the reaction of a methanolic copper(II) acetate solution and enantiomerically pure (5*R*)-/(5*S*)-methyl (*E*)-(4-ethyl-2-oxazolidinylidene)cyanoacetate **6**. This leads to microcrystalline products, which could be

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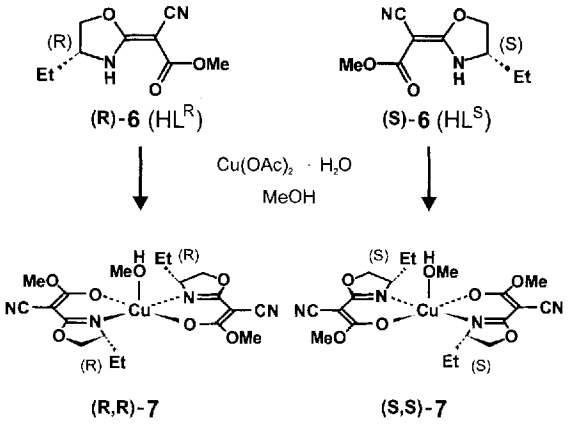
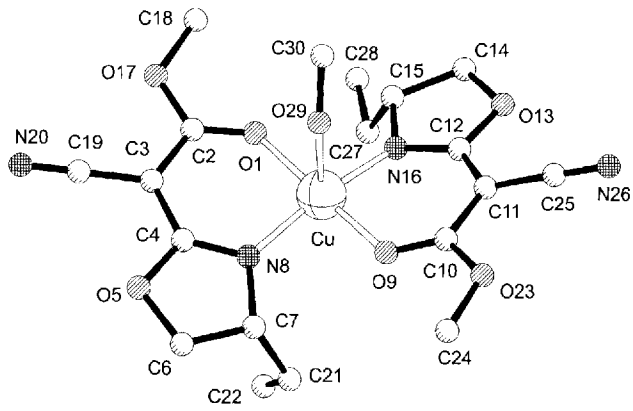


Figure 1. Structure of mononuclear complex (*R*,*R*)-7 with atomic numbering. H atoms omitted for clarity



recrystallized from methanol. According to their microanalyses, MS spectra and identical $\pm[\alpha]_D$-values, the products formed are the mononuclear bischelate complexes (*R*,*R*)-/(*S*,*S*)-**7**. In order to unequivocally determine the coordination geometry, we carried out an X-ray crystal structure analysis of (*R*,*R*)-**7**. The copper(II) center of (*R*,*R*)-**7** is coordinated as a slightly distorted tetragonal pyramid by two anions of (*R*)-**6** and methanol (Figure 1, Table 1, 2). The bond distances of the central copper atom to the enolato oxygens and oxazoline nitrogens, that form the tetragonal

Table 1. Crystal data, data collection and structure refinement for compounds (*R*,*R*)-**7**, (*P*)-**8** and (*M*)-**8**

	(*R*,*R*)-**7**	(*P*)-**8**	(*M*)-**8**
Empirical formula	$C_{19}H_{26}CuN_4O_7$	$C_{20}H_{24}Cl_6CuN_4O_6$	$C_{20}H_{24}Cl_6CuN_4O_6$
Molecular mass	485.98	692.67	692.67
Crystal system	tetragonal	monoclinic	monoclinic
Space group	*I*4	*P*2(1)	*P*2(1)
Cryst. size [mm]	0.25, 1.5, 0.3	0.15, 0.2, 0.25	0.3, 0.3, 0.2
a [Å]	25.286(1)	9.873(1)	9.815(2)
b [Å]		14.238(1)	14.189(3)
c [Å]	7.373(1)	10.422(1)	10.397(2)
α[°]	90	90	90
β [°]	90	94.302(6)	94.303(12)
γ [°]	90	90	90
V [Å^3]	4714.1(7)	1461.0(2)	1443.7(5)
ρ_{calc} [gcm^{-3}]	1.369	1.574	1.593
Z	8	2	2
T [K]	293(2)	293(2)	293(2)
Data collection			
Diffractometer	Siemens R4	Siemens P4	Nonius MACH3
Radiation	Mo-K_α, λ = 0.71073 Å, graphite monochromator		
Data collect. mode	ω-scans	ω-scans	ω/θ-scans
Theta range [°]	1.75-27.5	1.75-27.5	2.43-25.97
hkl range	0, 32/0, 32/0, 9	0, 12/ 0, 18/ -13, 13	-12, 12/ -17, 17/ -12, 12
Measured refl.	3055	4408	6220
Unique refl.	2926	3761	5641
Obsd. refl.	2376 [$F > 3\sigma(F)$]	3485 [$F > 3\sigma(F)$]	4511[$I > 2\sigma(I)$]
Absorption correction	ψ-scans	ψ-scans	ψ-scans
Refinement			
Solution by		direct methods	
Method of refinement	full matrix LSQ on F	full matrix LSQ on F	full matrix LSQ on F^2
Data to parameter ratio	8.52	10.47	16.89
R-values	0.069, 0.065 (R/R_w)	0.053, 0.055 (R/R_w)	0.0672, 0.1721 (R_1/wR_2)
ρ_{fin} (max/min) [eÅ^{-3}]	0.92/ 0.33	0.75/ 0.65	0.700/ -0.855
Programme	SHELXTL PLUS[a]	SHELXTL PLUS[a]	SHELXL 93[b]

[a] Ref.[20]. – [b] Ref.[21].

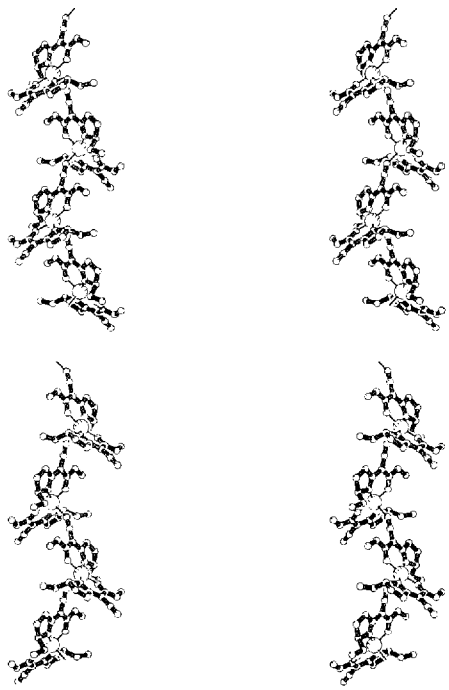
Table 2. Selected bond lengths (pm) and angles (°) of (*R*,*R*)-**7**

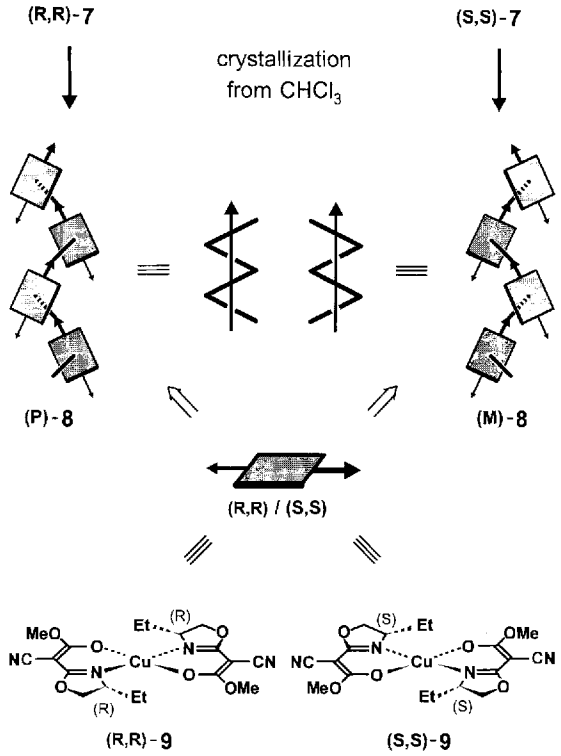
Distances	[pm]	Distances	[pm]	Distances	[pm]
Cu-O(1)	198.2(5)	Cu-N(8)	193.2(5)	Cu-O(9)	196.0(5)
Cu-N(16)	192.8(6)	Cu-O(29)	226.4(8)		
Angles	**[°]**	**Angles**	**[°]**	**Angles**	**[°]**
O(1)-Cu-N(8)	90.7(2)	O(1)-Cu-O(9)	176.6(3)	O(1)-Cu-O(29)	88.7(3)
N(8)-Cu-O(9)	89.2(2)	O(1)-Cu-N(16)	89.8(2)	O(9)-Cu-O(29)	87.9(3)
N(8)-Cu-N(16)	165.9(3)	O(9)-Cu-N(16)	91.1(2)	N(8)-Cu-O(29)	98.8(3)
N(16)-Cu-O(29)	95.3(3)				

plane, are 198.2 [Cu-O(1)], 196.0 [Cu-O(9)], 193.2 [Cu-N(8)], and 192.8 pm [Cu-N(16)]. Methanol occupies the sterically less hindered axial position with a Cu-O(29) distance of 226.4 pm.

According to our experience, recrystallization of mononuclear (*R*,*R*)-**7** from non-coordinating solvents should lead to the formation of a coordination polymer. Based on microanalytical data the dark green crystals which were obtained from chloroform had the general formula $\{[CuL^R_2] \cdot 2\ CHCl_3\}$, indicating loss of methanol. The X-ray crystal structure analysis of the copper(II) complex (*P*)-**8** clearly proves a well-ordered infinite one-dimensional architecture $^1_\infty[CuL^R_2]$ (*P*)-**8** (Figure 2, Table 1, 3). In accordance with this analysis, the crystal is composed of identical, palindromic (constant pitch)[7,16] strands with (*P*)-helicity. Each cylindrical strand is generated by a set of C_2-symmetric copper(II) building blocks (*R*,*R*)-**9**. The available structure data of (*P*)-**8** reveal that each of the copper atoms is linked across the N(26′) atom of only one neighbouring cyano group of the monomers (*R*,*R*)-**9**. The central copper atoms in $^1_\infty[CuL^R_2]$ (*P*)-**8** are almost tetragonal-pyramidally coordinated, with the planes of the two ligands L^R [HL^R = (*R*)-**6**]

Figure 2. Stereoview of crystal packing of helical coordination polymers **8**. Top: Right-handed helix (*P*)-**8**. Bottom: Left-handed helix (*M*)-**8**. For reasons of clarity H atoms and clathrate chloroform are omitted





twisted relative to each other to form an angle of 28.4° [torsion angle: angle between the perpendiculars of the planes O(1)-Cu-N(8) and O(9)-Cu-N(16)]. The Cu−N(26′) distance is 241.0 pm (Figure 3, Table 1, 3). Contrary to 3D-**1**, 2D-**2**, and 1D-polymer **3**, the monomers (*R*,*R*)-**9** in the helix polymer (*P*)-**8** are not positioned perpendicular to each other. The bond angle C(25)-N(26)-Cu′ in (*P*)-**8** has been

Figure 3. Structure of monomeric unit of helical coordination polymer (*P*)-**8**. H atoms omitted

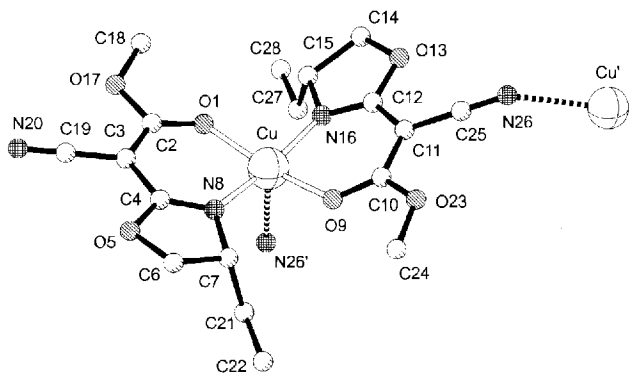


Table 3. Selected bond lengths (pm) and angles (°) of (*P*)-**8**

Distances	[pm]	Distances	[pm]	Distances	[pm]
Cu-O(1)	198.1(4)	Cu-N(8)	195.3(5)	Cu-O(9)	197.9(4)
Cu-N(16)	196.0(5)	Cu-N(26′)	241.0(6)		
Angles	**[°]**	**Angles**	**[°]**	**Angles**	**[°]**
O(1)-Cu-N(8)	90.1(2)	O(1)-Cu-O(9)	167.0(2)	O(1)-Cu-N(26′)	93.9(2)
N(8)-Cu-O(9)	89.4(2)	O(1)-Cu-N(16)	88.9(2)	O(9)-Cu-N(26′)	99.1(2)
N(8)-Cu-N(16)	168.9(2)	O(9)-Cu-N(16)	89.1(2)	N(8)-Cu-N(26′)	93.8(2)
N(16)-Cu-N(26′)	97.3(2)				
N(16)-Cu-N(26′)	97.3(2)				

found to be 146.8°, compared to almost 180° in **1** to **3**. The 1D-coordination polymer (*P*)-**8** cocrystallizes with chloroform to form a clathrate $^{1}_{\infty}\{[CuL^{R}_{2}]\ \ 2\ CHCl_3\}$ [stoichiometry: host/guest = (*R*,*R*)-**9**/$CHCl_3$ = 1/2].

The formation of 1D-coordination polymer (*P*)-**8** in chloroform is understandable, if one assumes as initial step backside attack at mononuclear (*R*,*R*)-**7** by one cyano group of a second molecule according to a S_N2 type mechanism. Repetitive substitution of methanol leads to the product $^{1}_{\infty}[CuL^{R}_{2}]$ (*P*)-**8**. Asymmetric induction of the stereogenic center of chiral enantiomerically pure (*R*)-**6** stereospecifically leads to *right-handed* helicity in polymer (*P*)-**8**.

Consequently, the mononuclear complex (*S*,*S*)-**7** was obtained starting from (*S*)-**6**, which on recrystallization from chloroform afforded *left-handed* 1D-coordination polymer (*M*)-**8**. The structure of $^{1}_{\infty}[CuL^{S}_{2}]$ (*M*)-**8** was determined by X-ray crystal structure analysis (Figure 2, Table 1)[17]. Each helix strand is composed of C_2-symmetric building blocks (*S*,*S*)-**9**.

In conclusion, we have demonstrated that stereogenic centers of ligands may stereospecifically induce helicity of 1D-coordination polymers. Thus (*R*)-**6** gives rise to (*P*)-**8** and (*S*)-**6** to mirror image (*M*)-**8**[11].

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Experimental Section

General: ^{1}H- and ^{13}C NMR spectra were obtained on a Jeol JNM-GX-400 (400 MHz; 100 MHz) spectrometer with TMS as internal standard. Chemical shifts are given in ppm. Mass spectra were recorded on a Varian MAT 3rA (EIMS) or on a Finnigan MAT TSQ 70 instrument (ion desorption from m-NBA matrix: 10 keV xenon atoms, FABMS). Specific Rotations were carried out on a Schmidt and Haensch polatronic E polarimeter. Melting points are not corrected. Microanalyses: Heraeus CHN-Mikroautomat. – IR: Perkin-Elmer 1420 Ratio-Recording Infrared Spectrophotometer.

Ligands: Methyl(5R,E)- and (5S,E)-(4-Ethyl-2-oxazolidinylidene)cyanoacetate **6**: (*R*)-/(*S*)-**6** were prepared following the literature methods cited[18] from 2.03 g (10 mmol) methyl 2-cyano-3,3-bis(methylsulfanyl)acrylate and 0.89 g (10 mmol) (*R*)-/(*S*)-2-amino-1-butanol. Yield: 1.74 g (88.7%). – M.p. 124°C. – IR (KBr): $\tilde{\nu}$ = 3430 cm^{-1} (NH), 2200 (C≡N), 1680 (C=O), 1590 (C=C). – ^{1}H NMR ([D$_6$]DMSO): δ = 0.82 (t, 3H, CH_3), 1.57, 1.69 (m, 2H, CH_2), 3.64 (s, 3H, OCH_3), 4.11 (m, 1H, CHN), 4.40, 4.69 (dd, 2H, CH_2O), 9.46 (s, 1H, NH). – ^{13}C NMR ([D$_6$]DMSO): δ = 8.35 (CH_3), 26.07 (CH_2), 50.85 (OCH_3), 53.71 (=C), 57.04 (CH), 73.13 (CH_2O), 117.04 (CN), 166.75, 170.06 (=CN, C=O). – MS (EI, 70 eV); *m/z* (%) = 196 [M$^+$]. – $C_9H_{12}N_2O_3$ (196.21): calcd. C 55.09, H 6.17, N 14.28; found C 54.85, H 6.09, N 14.44. – $[\alpha]_{546}$ = −23.3 (*R*)-**6**, +23.3 (*S*)-**6** (*c* = 0.03 g/ml, EtOH, 23°C).

Monomeric Complex (R,R)-7 and (S,S)-7: To a solution of 200 mg (1 mmol) $Cu(OAc)_2 \cdot H_2O$ in 40 ml of methanol, 392 mg (2 mmol) enantiomerically pure (*R*)-**6**, respectively, (*S*)-**6** were added. The green mixtures were stirred at 23°C for 4 h. The solvent was evaporated and the residues were crystallized from methanol. Yield: 472 mg (97%), light green needles. – M.p. >250°C (dec). – IR ($CHBr_3$): $\tilde{\nu}$ = 3470 cm^{-1} (OH), 2200 (C≡N), 1620, 1530, 1450 (C=C, C=N). – MS (EI, 70 eV); *m/z*: 487 [CuL_2^+ + ^{63}Cu − Et], 453 [CuL_2^+], 517 [CuL_2^+ + ^{63}Cu + H]. – FAB-MS; *m/z*: 454 [CuL_2^+ + H], 712 [$Cu_2L_3^+$ + H], 776 [$Cu_3L_3^+$ + H], 971 [$Cu_4L_3^+$ + 2H][19]. – $C_{19}H_{26}CuN_4O_7$ (485.98): calcd. C 46.96, H 5.39, N 11.53; found C 46.86, H 5.37, N 11.57. – $[\alpha]_{546}$ = +1000 [(*R*)-**6**], −1000 [(*S*)-**6**] (*c* = 0.001 g/ml, $CHCl_3$, 23°C).

Helix Coordination Polymers (P)-/(M)-8: 49 mg (0.1 mmol) of the monomeric complex (*R*,*R*)-**7**, respectively, (*S*,*S*)-**7** was dissolved in 10 ml $CHCl_3$ at 60°C. The hot solution was filtered and after a few days standing at 23°C dark green prisms were formed. Yield: 58 mg (83%). – M.p. 244°C (dec). – IR ($CHBr_3$): $\tilde{\nu}$ = 2200 cm^{-1} (C≡N), 1620, 1530, 1450 (C=C, C=N). – MS (EI, 70 eV); *m/z*: 487 [CuL_2^+ + ^{63}Cu − Et], 453 [CuL_2^+], 516 [CuL_2^- + ^{63}Cu]. – MS (FAB, m-NBA); *m/z*: 454 [CuL_2^+ + H], 712 [$Cu_2L_3^+$ + H], 776 [$Cu_3L_3^+$ + H], 971 [$Cu_4L_3^+$ + 2H]. – $C_{20}H_{24}Cl_6CuN_4O_6$ (692.70): calcd. C 34.68, H 3.49, N 8.09; found C 35.06, H 3.56, N 8.21.

Crystallographic Analyses: The crystal structures of the monomeric complex (*R*,*R*)-**7** and the helical polymers (*P*)-**8** and (*M*)-**8** have been determined by single crystal X-ray diffraction studies. Crystal and structure solution and refinement data are summarized in Table 1, the molecular structures are shown in Figure 1–3. Important bond lengths and bond angles of (*R*,*R*)-**7** and (*P*)-**8** are shown in Tables 2 and 3.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100211 [(*R*,*R*)-**7**, (*P*)-**8**] and CCDC-100170 [(*M*)-**8**]. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

☆ Dedicated to Professor *Wolfgang Beck* on the occasion of his 65th birthday.

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