Coordination Polymers, 14[‡]

1D- and 2D-Coordination Polymers from Self-Complementary Building Blocks: Co-Crystallization of (*P*)- and (*M*)-Single-Stranded Diastereoisomers

Rolf W. Saalfrank,*[a] Harald Maid,[a] Frank Hampel,[a] and Karl Peters[b]

Dedicated to Prof. Dr. W.-P. Fehlhammer on the occasion of his 60th birthday

Keywords: Coordination polymers / Helical structures / Copper / Self-assembly / Supramolecular chemistry

Reaction of methanolic copper(II) acetate solution with oxazolidine **21** (HL^7) led to the formation of the one-dimensional coordination polymer 1D-$^1_\infty$[CuL$^7_2$] **23**. On the contrary, reaction of copper(II) acetate in methanol with pyrrolidine **24** (HL^8) yielded the two-dimensional coordination polymer 2D-$^2_\infty$[CuL$^8_2$] **26**. A common feature of **23** and **26** are the C_{2h}-symmetric coordinatively unsaturated building blocks **22** and **25**. In 1D-$^1_\infty$[CuL$^7_2$] **23**, the cyano groups are linked to copper in a *side-on* fashion and the monomers **22** are oriented parallel to one another, whereas in 2D-$^2_\infty$[CuL$^8_2$] **26** the cyano groups are bound to copper in the *end-on* mode and the monomers **25** are oriented at an angle of 117° to one another. In both 1D-**23** and 2D-**26**, copper has a distorted octahedral coordination sphere. On the other hand, reaction of methanolic copper(II) acetate solution with enantiomerically pure (5*S*)-pyrrolidine **27** (HL$^{9(S)}$) led to the formation of the diastereomeric helical strands (*M*)-/(*P*)-1D-$^1_\infty$[CuL$^{9(S)}_2$] **29**. (*M*)- and (*P*)-**29** are present in pairs in the infinite unit cell. In helical 1D-**29**, copper is tetragonal-pyramidally coordinated and the C_2-symmetric monomers **28** (CuL$^{9(S)}_2$) are linked through only one cyano group. Moreover, it has been shown that the reaction of chiral racemic pyrrolidine **30** (HL$^{10(R,S)}$) with copper(II) acetate via the intermediate C_i-symmetric building blocks **31** (CuL$^{10(R)}$L$^{10(S)}$) furnishes one-dimensional 1D-$^1_\infty$[CuL$^{10(R)}$-L$^{10(S)}$] **32**. Single-crystal X-ray diffraction analyses of the supramolecular species **23**, **26**, **29**, and **32** unequivocally establish the structures of these coordination polymers.

Introduction

With the growing understanding of supramolecular chemistry,[1] it might ultimately become feasible to routinely design and control solid-state architectures and therefore function.[2] Increasingly, solid structures are being invented and created rather than discovered. Realisation of such macromolecular targets requires the ability to assemble small supramolecular units that can be further aggregated in a controlled fashion. In order to construct such assemblies, we have developed coordinatively unsaturated building blocks of copper(II) and iron(II) with two additional ligating sites that do not interfere with the monomer assembly process but facilitate controlled aggregation.

We have recently shown that reaction of methanolic copper(II) acetate solution with tetrazole **8** (HL^1) leads to the formation of the three-dimensional coordination polymer 3D-$^3_\infty$[CuL$^1_2$] **1**,[3] whereas under exactly the same conditions pyrrolidine **9** (HL^2) forms the two-dimensional coordination polymer 2D-$^2_\infty$[CuL$^2_2$] **2**.[4] A prerequisite for the formation of 3D-**1** and 2D-**2** is the intermediate generation of the coordinatively unsaturated copper(II) building blocks **14** (L = L^1) and **15** (L = L^2). The monomers **14** and **15** are bidentate and coordinate through the two cyano groups. This leads to *perpendicular* linking of the monomers and to coordinative saturation at the copper(II) centers of **14** and **15** with formation of the corresponding three- and two-dimensional coordination polymers **1** and **2**. Thus, during the crystallization of the polymers **1** and **2**, the role of the building blocks **14** and **15** is twofold. They react both as metals and as ligands.[5] The exact structures of **1** and **2** were established by single-crystal X-ray analyses. In both polymers, the coordination sphere about the copper(II) atoms is a slightly distorted tetragonal bipyramid.

Unexpectedly, reaction of methanolic copper(II) acetate solution with tetrazole **10** (HL^3) furnished the coordination polymer 1D-$^1_\infty$[CuL$^3_2$] **3**. In the case of **3**, a *parallel* rather than a *perpendicular* orientation of the building blocks **16** (L = L^3) leads to one-dimensionality.[6] A one-dimensional zigzag coordination polymer 1D-$^1_\infty$[CuL$^4_2$] **4** was also obtained starting from benzoxazolidine **11** (HL^4). The reduced dimensionality of **4** allows **17** (L = L^4) to coordinate to copper(II) through one cyano group only.[7]

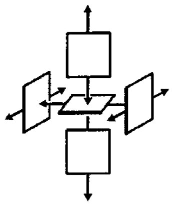
In contrast to the C_{2h}-symmetric monomers **14−17**, the C_2-symmetric building block (*S*,*S*)-**18** (L = L$^{5(S)}$), generated from (*S*)-methoxycarbonylpyrrolidine **12** (HL$^{5(S)}$), is sterically shielded at one side and thus couples only through

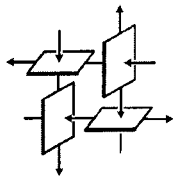
---

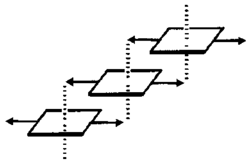
[‡] Part 13: Ref.[12]

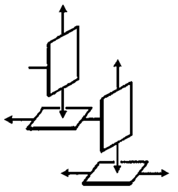
[a] Institut für Organische Chemie der Universität Erlangen-Nürnberg,
Henkestraße 42, D-91054 Erlangen, Germany
Fax: (internat.) +49-(0)9131/852-1165
E-mail: saalfrank@organik.uni-erlangen.de
[b] Max-Planck Institut für Festkörperforschung,
Heisenbergstraße 1, D-70506 Stuttgart, Germany

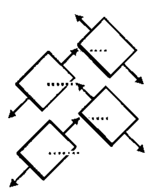
1434−1948/99/1111−1859 $ 17.50+.50/0


3D-$^{3}_{\infty}$[CuL$^{1}_{2}$] **1**

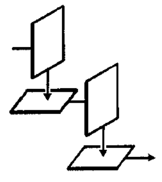

2D-$^{2}_{\infty}$[CuL$^{2}_{2}$] **2**


1D-$^{1}_{\infty}$[CuL$^{3}_{2}$] **3**

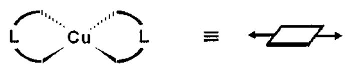

1D-$^{1}_{\infty}$[CuL$^{4}_{2}$] **4**


(*M*)-1D-$^{1}_{\infty}$[CuL$^{5(S)}_{2}$] **5**

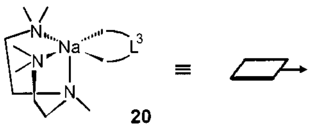
(*M*)-1D-$^{1}_{\infty}$[CuL$^{6(S)}_{2}$] **6**


$_{\infty}$[(PMDETA)NaL] **7**

8 - 13



14 - 19



20

8 (HL^{1}): X = NCMe$_3$; Y–Z = N=N, R = CMe$_3$

9 (HL^{2}): X, Y, Z = CH$_2$; R = Me

10 (HL^{3}): X = NCH$_2$CHMe$_2$; Y–Z = N=N, R = M

11 (HL^{4}): X = O; Y–Z = C$_6$H$_4$; R = Me

12 (HL$^{5(S)}$): X, Y = CH$_2$; Z = (*S*)-CHCO$_2$Me; R = M

13 (HL$^{6(R/S)}$): X = O; Y = CH$_2$; Z = (*R*/*S*)-CHEt; R = M

14: L = L^{1}

15: L = L^{2}

16: L = L^{3}

17: L = L^{4}

18: L = L$^{5(S)}$

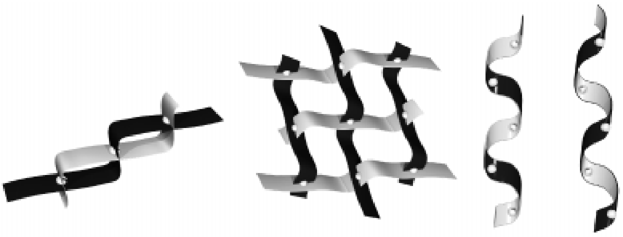
19: L = L$^{6(R/S)}$

one cyano group. This leads to the helical one-dimensional coordination polymer 1D-$^{1}_{\infty}$[CuL$^{5(S)}_{2}$] **5**. According to the X-ray diffraction analysis, the crystal is composed of two almost identical helix strands, (*P*)-1D-$^{1}_{\infty}$[CuL$^{5(S)}_{2}$] **5** and (*M*)-1D-$^{1}_{\infty}$[CuL$^{5(S)}_{2}$] **5**,[8] which generate pairs of diastereoisomers.[9] It is noteworthy that the stereogenic centers in (*S*,*S*)-**18** do not lead to asymmetric induction. Racemic mixtures of single-stranded coordination polymers with (*P*)- and (*M*)-helicity were also obtained with achiral ligands and copper(I).[10]

To date, only a few examples of chiral, non-racemic helical coordination polymers have been reported, where the chirality is induced by a stereogenic center.[11][12] For example, reaction of a methanolic solution of enantiomerically pure oxazolidines **13** (HL$^{6(R/S)}$) with copper(II) acetate and crystallization from chloroform afforded single-crystals suitable for X-ray diffraction analysis. This analysis showed the crystals to be composed of identical, palindromic one-dimensional strands (*P*)-1D-$^{1}_{\infty}$[CuL$^{6(R)}_{2}$] **6** and (*M*)-1D-$^{1}_{\infty}$[CuL$^{6(R)}_{2}$] **6**.[8][13] Each cylindrical strand is formed by a set of C_2-symmetric copper(II) building blocks (*R*,*R*)-**19** (L = L$^{6(R)}$) and (*S*,*S*)-**19** (L = L$^{6(S)}$).

Regardless of steric considerations, by using a Group 1 metal, the zigzag one-dimensional coordination polymer 1D-$^{1}_{\infty}$[(PMDETA)NaL^{3}] **7** was formed. The polymer **7** is generated from the coordinatively unsaturated building block [(PMDETA)NaL^{3}] **20**.[14]

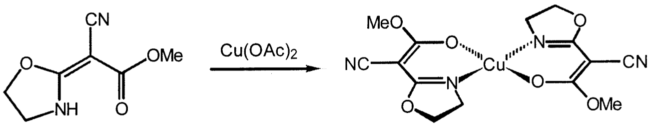
We report here on the synthesis of the one-dimensional coordination polymers 1D-$^{1}_{\infty}$[CuL$^{7}_{2}$] **23** and 1D-$^{1}_{\infty}$[CuL$^{10(R)}$L$^{10(S)}$] **32**, the two-dimensional coordination polymer 2D-$^{2}_{\infty}$[CuL$^{8}_{2}$] **26**, and the helical coordination polymer strands (*P*)-/(*M*)-1D-$^{1}_{\infty}$[CuL$^{9(S)}_{2}$] **29**, which generate pairs of diastereoisomers in the infinite unit cell.[15]


23, 32 **26** **29**

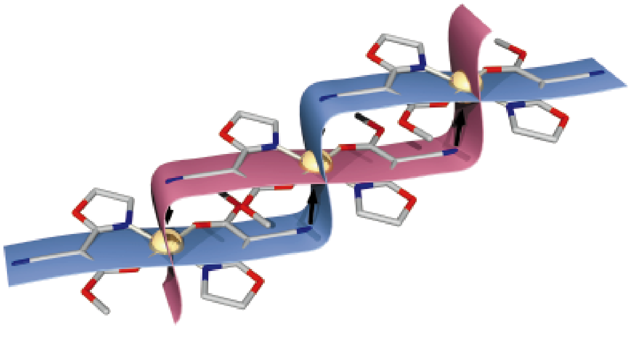
Results and Discussion

One-Dimensional Coordination Polymer 1D-$^{1}_{\infty}$[CuL$^{7}_{2}$] (23)

Reaction of a solution of NH-acidic oxazolidine **21** (HL^{7})[16][17] with copper(II) acetate in methanol yielded dark-green microcrystals.



HL^{7} **21** CuL$^{7}_{2}$ **22**


1D-$^{1}_{\infty}$[CuL$^{7}_{2}$] **23**

On the basis of elemental analysis data and an X-ray diffraction study, the product was identified as the one-dimensional coordination polymer 1D-$^{1}_{\infty}$[CuL$^{7}_{2}$] **23**. The construc-

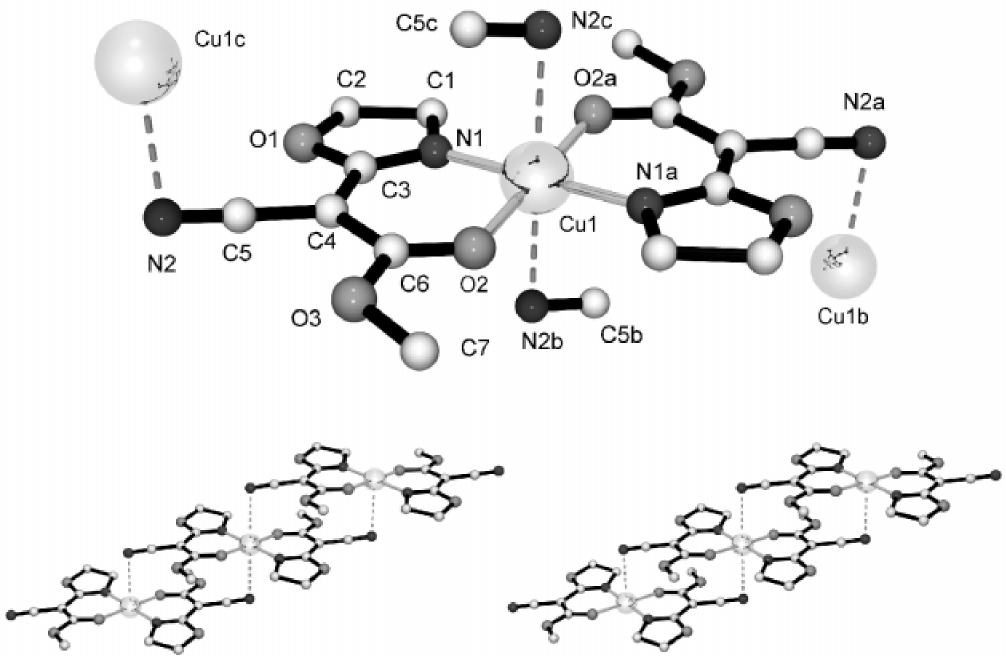


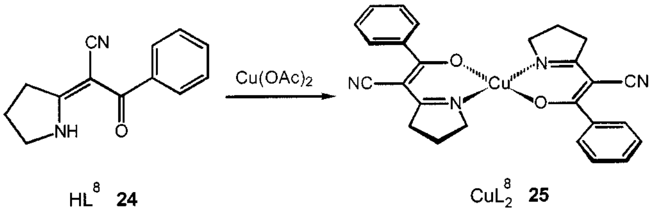
Figure 1. Top: structure of monomeric unit **22** of one-dimensional coordination polymer 1D-$^{1}_{\infty}$[CuL$^{7}_{2}$] **23** showing atomic numbering; H atoms omitted for clarity; bottom: stereoview of **23** in the infinite unit cell

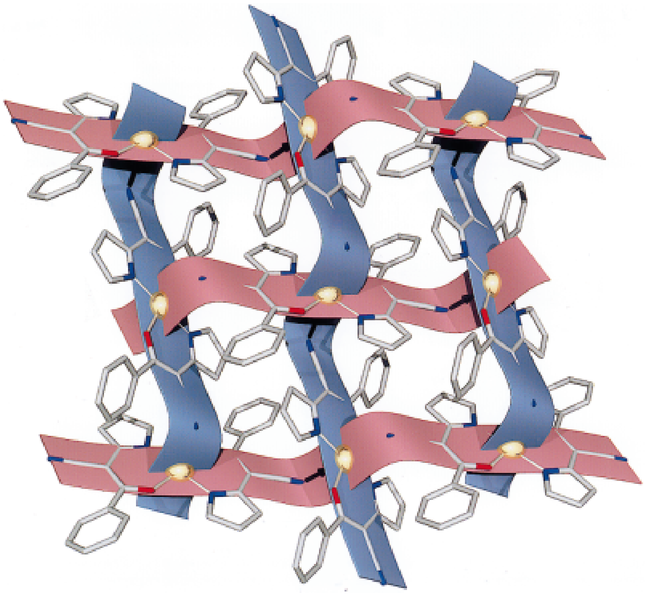
tion of **23** becomes clear if one assumes the formation and linkage of the self-complementary building blocks **22** (Cu L$^{7}_{2}$). Intermediate **22** is coordinatively unsaturated and is also bis-monodentate with respect to the two CN groups. Specifically, the C_{2h}-symmetric monomers **22** are aligned parallel to one another. The equatorial cyano groups are coupled to copper in a *side-on* fashion with a Cu(1c)−N(2)−C(5) angle of 99.84° (Figure 1). The d^{9}-Cu^{II} ions are six-fold coordinated and are located in the center of a square-planar bipyramid. The Cu(1c)−N(2) distance amounts to 291.0 pm.

Two-Dimensional Coordination Polymer 2D-$^{2}_{\infty}$[CuL$^{8}_{2}$] (26)

In order to study the effect of the ligands on the dimensionality of the coordination polymers, we treated a methanolic solution of pyrrolidine **24** (HL^{8})[16][18] with copper(II) acetate and isolated a green precipitate, which dissolved most readily in coordinating solvents. According to the microanalytical data and a single-crystal X-ray diffraction analysis, the two-dimensional coordination polymer 2D-$^{2}_{\infty}$[CuL$^{8}_{2}$] **26** was formed.

Polymer **26** is generated from the coordinatively unsaturated C_{2h}-symmetric building blocks **25** (CuL$^{8}_{2}$) along the two cyano groups. This leads to coordinative saturation at the copper(II) centers through distorted tetragonal bipyramids (Figure 2). The Cu(a)−N(10) distance measures 277.1 pm. The cyano groups of monomer **25** are bound to copper with a Cu(a)−N(10)−C(9) angle of 117.0°. The Cu−Cu distances amount to 759.9 pm (coplanar) and 992.3 pm (interplanar).





2D-$^{2}_{\infty}$[CuL$^{8}_{2}$] **26**

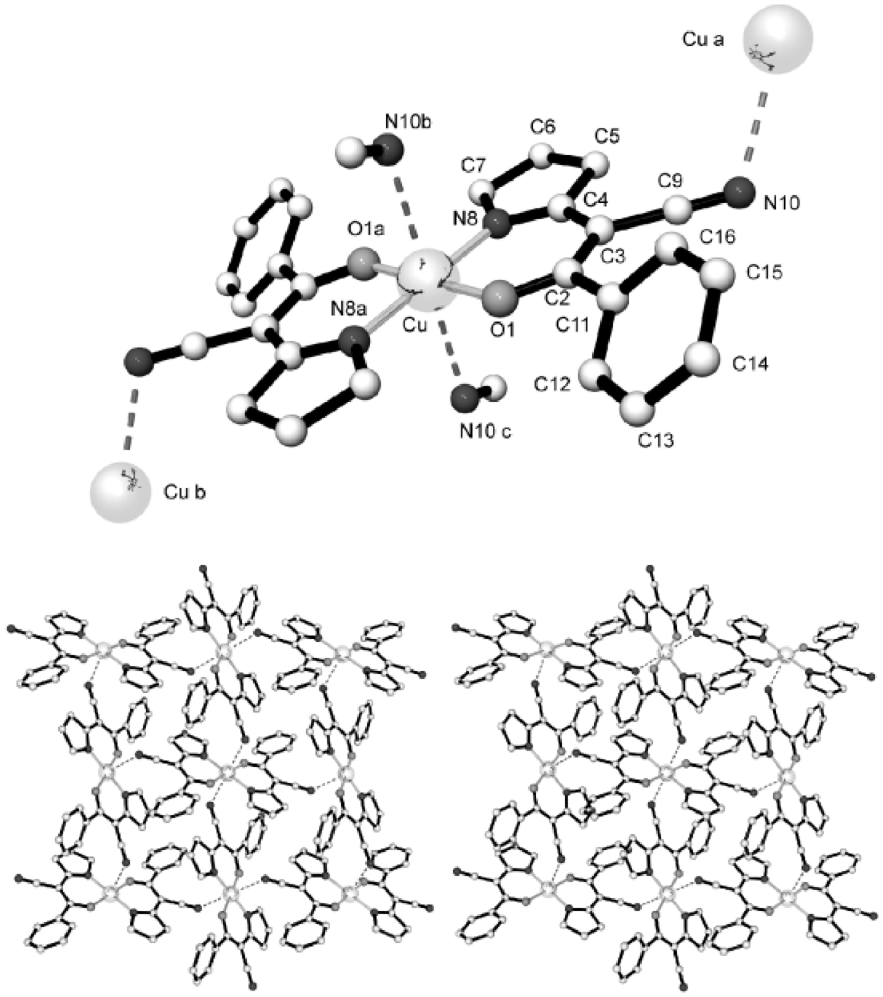
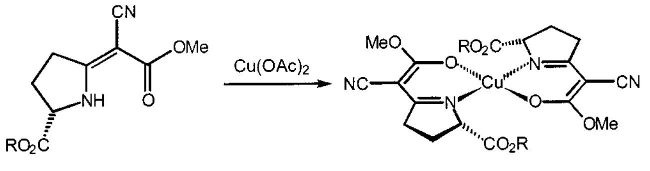


Figure 2. Top: structure of monomeric unit **25** of two-dimensional coordination polymer 2D-$^{2}_{\infty}$[CuL$^{8}_{2}$] **26** showing atomic numbering; H atoms omitted for clarity; bottom: stereoview of **26** in the infinite unit cell

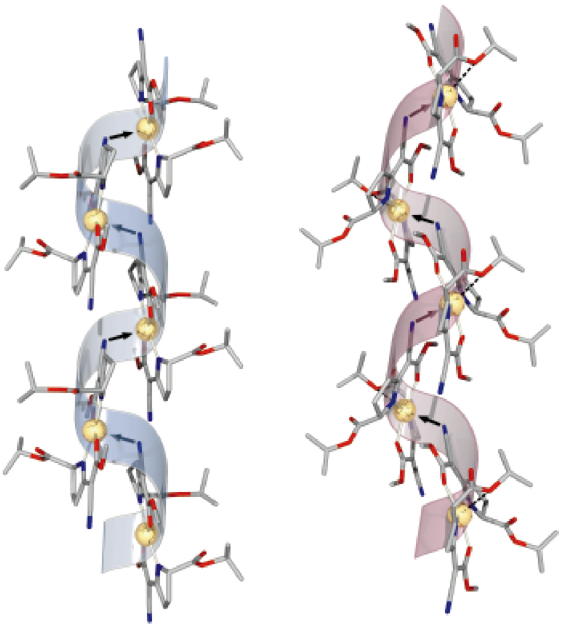
Helical Strands (M)-/(P)-1D-$^{1}_{\infty}$[CuL$_2^{9(S)}$] (29)

Reaction of a methanolic copper(II) acetate solution and (*S*)-isopropyloxycarbonylpyrrolidine **27** (HL$^{9(S)}$)[16] in the presence of triethylamine furnished light-green needles. According to the stoichiometric composition and an X-ray crystal structure analysis, the product obtained consisted of the helical coordination polymer (*M*)-/(*P*)-1D-$^{1}_{\infty}$[CuL$_2^{9(S)}$] **29**.[19]

The formation of the one-dimensional coordination polymer **29** can be rationalized if one assumes the intermediate generation of the coordinatively unsaturated C_2-symmetric building block [CuL$_2^{9(S)}$] **28**, which is sterically shielded at one side by two isopropyloxycarbonyl groups. Therefore, in



HL$^{9(S)}$ **27** R = CHMe$_2$ CuL$_2^{9(S)}$ **28**



(*M*)-/(*P*) -1D-$^{1}_{\infty}$[CuL$_2^{9(S)}$] **29** contrast to 1D-$^{1}_{\infty}$[CuL$^{7}_{2}$] **23**, where copper displays tetragonal-bipyramidal coordination, attack of **28** through only one cyano group is possible. This leads to tetragonal-pyramidal coordination at the copper(II) centers with formation of **29**. The infinite unit cell is composed of helix strands made up of pairs of the diastereoisomers (*M*)-/(*P*)-1D-$^{1}_{\infty}$[Cu L$^{9(S)}_{2}$] **29**.

It is noteworthy that the stereogenic centers of the chiral C_2-symmetric monomers [CuL$^{9(S)}_{2}$] **28** did not induce asymmetry in favour of either an (*M*)- or a (*P*)-helix. Each strand is composed of a set of identical monomeric building blocks **28**, which differ considerably in their bond lengths and angles. The available structural data for the monomeric units (*M*)-**28** [Figure 3 (a)] and (*P*)-**28** [Figure 3 (b)] reveal that each of the Cu atoms of the helical diastereoisomers (*M*)-**29** [Figure 3 (c)] and (*P*)-**29** [Figure 3 (d)] is linked through the nitrogen atom of only one neighbouring cyano group of the monomers. The central Cu atoms in (*M*)-**29** and (*P*)-**29** are almost tetragonal-pyramidally coordinated, with the planes of the two ligands L$^{9(S)}$ (HL$^{9(S)}$ = **27**) twisted with respect to one another to form angles of 7.97° and 13.64° [torsion angles: angles between the perpendiculars of the planes O(1)−Cu(1)−N(1), O(5)−Cu(1)−N(3), and O(9)−Cu(1)−N(5), O(13)−Cu(1)−N(7), respectively]. The distances Cu(1)−N(2a) and Cu(2)−N(8a) are 259.3 pm in (*M*)-**29** and 265.3 pm in (*P*)-**29**. The bond angles C(3Aa)−N(2a)−Cu(1) and C(301a)−N(8a)−Cu(2) are found to be 114.0° in (*M*)-**29** and 127.4° in (*P*)-**29**, respectively. The main difference between (*M*)-**28** and (*P*)-**28** is the short distance of 301.8 pm between Cu(2) and O(12) in (*P*)-**28**.

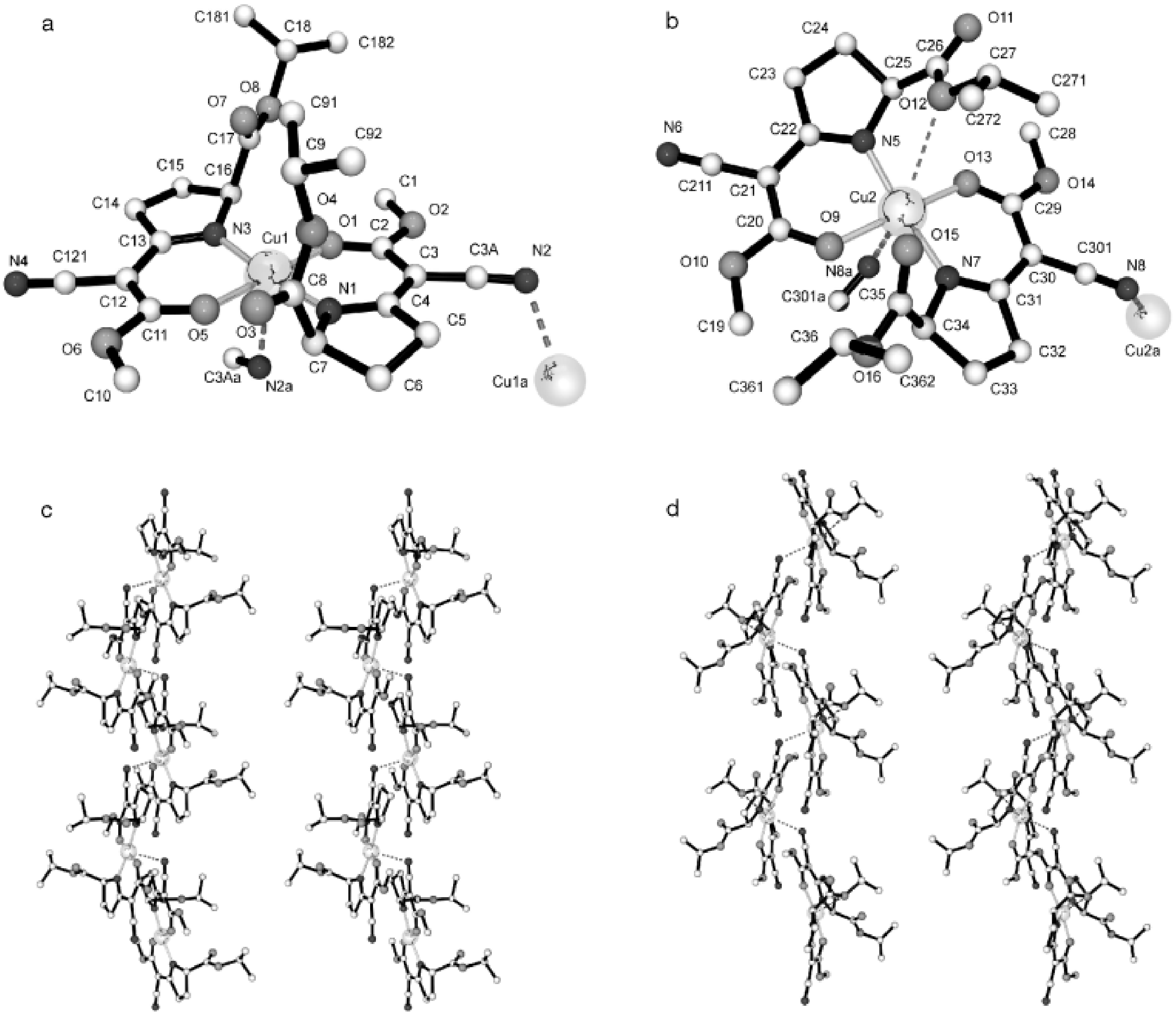
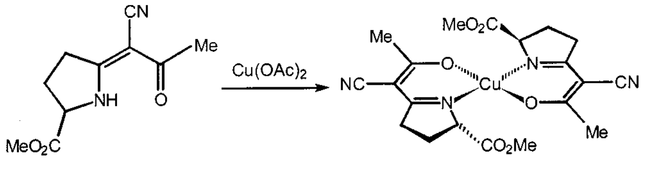


Figure 3. Top: structure of the monomeric units (*M*)-**28** (a) and (*P*)-**28** (b) showing atomic numbering of the helical diastereoisomers (*M*)-/(*P*)-1D-$^{1}_{\infty}$[CuL$^{9(S)}_{2}$] **29**; H atoms omitted for clarity; bottom: stereoview of **29** in the infinite unit cell (c) (*M*)-**29**, (d) (*P*)-**29**

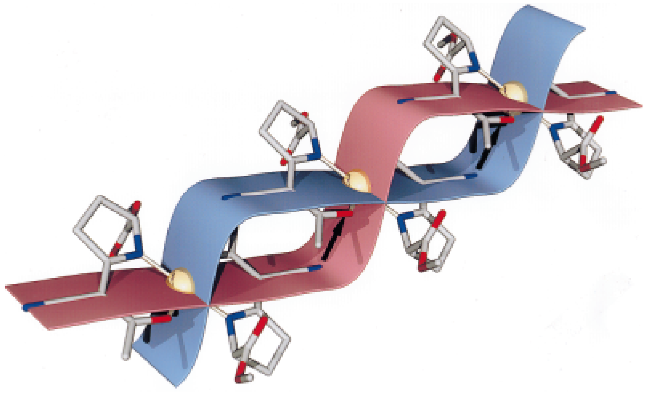
One-Dimensional Coordination Polymer 1D-$^{1}_{\infty}$[CuL$^{10(R)}$L$^{10(S)}$] (32)

In contrast to enantiomerically pure pyrrolidine **27** (HL$^{9(S)}$), which led via the C_2-symmetric intermediate **28** to the helical strands (*M*)-/(*P*)-1D-$^{1}_{\infty}$[CuL$_2^{9(S)}$] **29**, reaction of a methanolic solution of NH-acidic, chiral, racemic pyrrolidine **30** (HL$^{10(R,S)}$) with copper(II) acetate afforded the C_i-symmetric coordinatively unsaturated building block (CuL$^{10(R)}$L$^{10(S)}$) **31**. Dipole−cation interaction between the CN groups and the copper(II) centers of the key intermediates **31** yielded the one-dimensional coordination polymer 1D-$^{1}_{\infty}$[CuL$^{10(R)}$L$^{10(S)}$] **32**.



HL$^{10(R,S)}$ **30**

CuL$^{10(R)}$L$^{10(S)}$ **31**



1D-$^{1}_{\infty}$[CuL$^{10(R)}$L$^{10(S)}$] **32**

The monomers **31** are aligned parallel to one another and the equatorial cyano groups of **31** are directed towards the copper in a *side-on* fashion with a Cu(1a)−N(2)−C(4) angle of 111.6° (Figure 4). The d^9-Cu(II) ions are six-fold coordinated and are located in the center of a square plane. The Cu(1)−N(2b) distance of 354.6 pm in **32** is rather long compared with that of 291.0 pm in **23** (Figure 1).

Conclusions

The high degree of symmetry of the coordination polymers obtained through spontaneous organization of the self-complementary building blocks **22** and **25** (C_{2h}), **28** (C_2), and **31** (C_i) is surprising. However, we are far from being able to foresee structures such as the one-dimensional coordination polymers 1D-$^{1}_{\infty}$[CuL$_2^7$] **23** and 1D-$^{1}_{\infty}$[CuL$^{10(R)}$L$^{10(S)}$] **32**, the two-dimensional sheets 2D-$^{2}_{\infty}$[CuL$_2^8$] **26**, or the helical strands (*M*)-/(*P*)-1D-$^{1}_{\infty}$[CuL$_2^{9(S)}$] **29**, which generate pairs of diastereoisomers in the infinite unit cell. The present study on the use of self-complementary building blocks for the construction of coordination polymers suggests that more experimental endeavour is necessary in order to be able to predict the dimensionality of these potential materials.

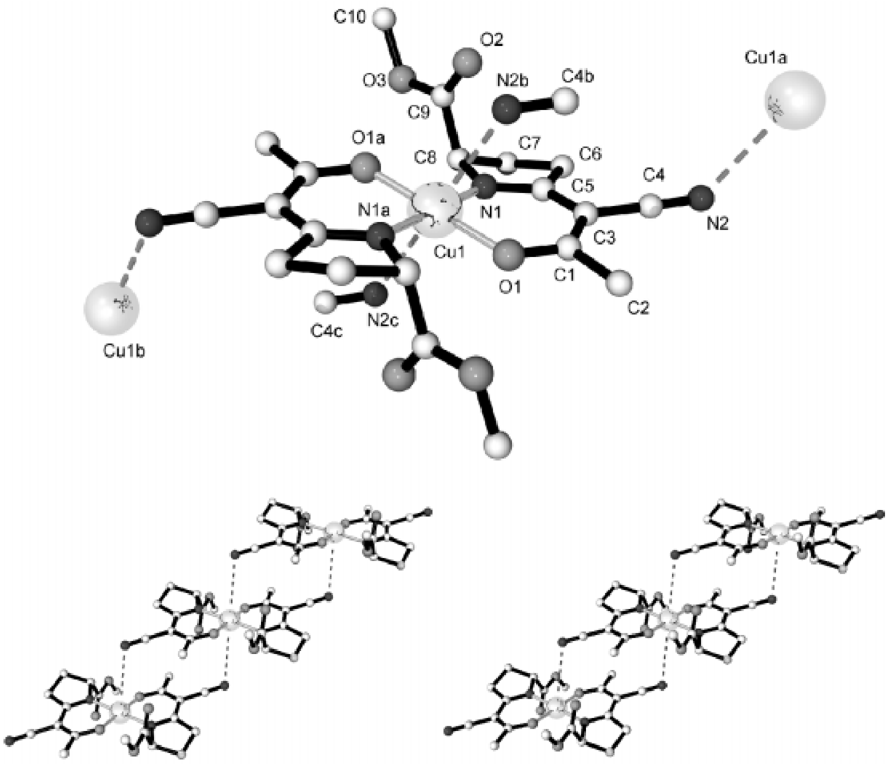


Figure 4. Top: structure of monomeric unit **31** of one-dimensional coordination polymer 1D-$^{1}_{\infty}$[CuL$^{10(R)}$L$^{10(S)}$] **32** showing atomic numbering; H atoms omitted for clarity; bottom: stereoview of **32** in the infinite unit cell

Experimental Section

Materials and Methods: All common reagents and solvents were purchased from commercial suppliers and were used without further purification unless otherwise indicated. − Melting points were determined on a Wagner−Munz apparatus and are uncorrected. − Infrared spectra were recorded on a Beckman Acculab or on a Perkin−Elmer 1420 ratio recording infrared spectrophotometer. − ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM-GX-400 spectrometer at 400 and 100.5 MHz, respectively. The carbon atoms were assigned with the aid of the DEPT technique. All chemical shifts are based on the δ scale, referenced to TMS as an internal standard. − Mass spectra were recorded on a Varian MAT311 A (EIMS) or on a micromass ZabSpec (ion-desorption from a *m*-nitrobenzyl alcohol matrix: 8 keV, caesium atoms FAB-MS).

General Procedure for the Synthesis of the Vinylogous Amide Ligands 21, 24, 27, and 30:[16] A stirred mixture of a cyclic imino ether and the corresponding β-oxo nitrile (for quantitative proportions, refer to specific cases) was heated for 24 h at 100 °C. Ethanol, formed during the reaction, was distilled off (in a stream of nitrogen in the case of **27** and **30**). The hot reaction mixture was then filtered, cooled to 20 °C, and the excess starting materials were recovered by distillation under reduced pressure. The brownish crude product was washed with cold methanol. Colourless crystals were obtained from methanol.

Methyl (*E*)-2-Cyano-2-(oxazolidine-2-ylidene)acetate (21): Prepared from 4,5-dihydro-2-ethyloxyoxazole[16] (4.6 g, 40 mmol) and methyl cyanoacetate (15.8 g, 160 mmol). Yield: 4.2 g (62%); m.p. 144 °C. − ^{1}H NMR (400 MHz, $CDCl_3$/[D$_6$]DMSO, 5:1, 25 °C): δ = 3.75 (s, 3 H, CH_3), 3.93 [t, ^3J(H,H) = 8.3 Hz, 2 H, $C_{(4)}H_2$], 4.72 [t, ^3J(H,H) = 8.3 Hz, 2 H, $C_{(5)}H_2$], 8.72 (br. s, 1 H, NH). − ^{13}C NMR (100.5 MHz, $CDCl_3$/[D$_6$]DMSO, 5:1, 25 °C): δ = 43.67 ($C_{(4)}$), 51.56 (CH_3), 55.92 (=*C*−CN), 69.50 ($C_{(5)}$), 116.67 (CN), 168.34, 172.07 (C=O or $C_{(2)}$). − IR ($CHBr_3$): ṽ = 3320 (NH), 2940 (CH), 2200 (C≡N), 1670 (C=O), 1590 cm^{-1} (C=C). − MS (70 eV, EI): *m*/*z* (%): 168 [M$^+$] (30).

(*Z*)-2-Cyano-2-(pyrrolidine-2-ylidene)-1-phenylethanone (24):[18] Prepared from 5-ethyloxy-3,4-dihydro-2*H*-pyrrole[16] (4.1 g, 36 mmol) and benzoylacetonitrile (1.3 g, 9 mmol). Yield: 1.7 g (89%); m.p. 145 °C. − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.09 (br. q, 2 H, $C_{(4)}H_2$), 3.02 (br. t, 2 H, $C_{(3)}H_2$), 3.72 (br. t, 2 H, $C_{(5)}H_2$), 7.40−7.49 (m, 3 H, Ar $C_{(3,4,5)}$H), 7.79−7.87 (m, 2 H, Ar $C_{(2,6)}$H), 10.89 (br. s, 1 H, NH). − ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 20.23 ($C_{(4)}$), 34.13 ($C_{(3)}$), 49.80 ($C_{(5)}$), 77.63 (=*C*−CN), 121.00 (C≡N), 127.78, 128.09 (Ar $C_{(3,4,5)}$), 131.25 (Ar $C_{(2,6)}$), 138.91 (Ar $C_{(1)}$), 176.03 ($C_{(2)}$), 190.88 (C=O). − IR (KBr): ṽ = 3280 (NH), 3030 (CH), 2190 (C≡N), 1620 (C=O), 1585, 1490 cm^{-1} (C=C). − MS (70 eV, EI): *m*/*z* (%): 212 [M$^+$] (50).

Methyl (*Z*)-2-Cyano-2-[(2*S*)-2-isopropyloxycarbonylpyrrolidine-5-ylidene]acetate (27): Prepared from (2*S*)-5-ethyloxy-2-isopropyloxycarbonyl-3,4-dihydro-2*H*-pyrrole (15 g, 75 mmol) and methyl cyanoacetate (30 g, 300 mmol). Yield: 15.6 g (82%); m.p. 130 °C. − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.28, 1.29 [d, ^3J(H,H) = 6.0 Hz, 3 H, CH_3], 2.18−2.27 (m, 1 H, $C_{(3)}H_A$), 2.43−2.52 (m, 1 H, $C_{(3)}H_B$), 2.93−3.08 (m, 2 H, $C_{(4)}H_2$), 3.77 (s, 3 H, OCH_3), 4.54 [dd, ^3J(H,H) = 8.8 Hz, ^3J(H,H) = 5.5 Hz, 1 H, $C_{(2)}$H], 5.07 [sept., ^3J(H,H) = 6.1 Hz, 1 H, CH], 9.16 (br. s, 1 H, NH). − ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 21.81 (2 CH_3), 25.44 ($C_{(3)}$), 32.60 ($C_{(4)}$), 51.77 (OCH_3), 62.60 ($C_{(2)}$), 68.83 (=*C*−CN), 70.15 (OCH), 118.27 (C≡N), 167.93, 170.01, 173.63 (2 C=O or $C_{(5)}$). − IR ($CHBr_3$): ṽ = 3332 (NH), 2980, 2950 (CH), 2207 (C≡N), 1736, 1677 (C=O), 1592 cm^{-1} (C=C). − MS (70 eV, EI): *m*/*z* (%): 252 [M$^+$] (12).

(*Z*)-1-Cyano-1-(2-methoxycarbonylpyrrolidine-5-ylidene)propan-2-one (30): Prepared from β-oxobutyronitrile[20] (7.1 g, 86 mmol) and (2*S*)-5-ethyloxy-2-methoxycarbonyl-3,4-dihydro-2*H*-pyrrole (29.6 g, 173 mmol). Yield: 2.8 g (16%); m.p. 117 °C. − ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.22−2.32 (m, 1 H, $C_{(3)}H_A$), 2.41−2.51 (m, 1 H, $C_{(3)}H_B$), 2.33 (s, 3 H, CH_3), 2.94−3.10 (m, 2 H, $C_{(4)}H_2$), 3.78 (s, 3 H, OCH_3), 4.63 [dd, ^3J(H,H) = 8.9 Hz, ^3J(H,H) = 5.3 Hz, 1 H, CH], 10.61 (br. s, 1 H, NH). − ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 24.60 ($C_{(3)}$), 27.80 (CH_3), 32.59 ($C_{(4)}$), 52.87 (OCH_3), 62.53 ($C_{(2)}$), 80.09 (=*C*−CN), 119.79 (C≡N), 170.38, 173.32 (O−C=O or $C_{(5)}$), 195.12 (C=O). − IR ($CHBr_3$): ṽ = 3230 (NH), 2990, 2940 (CH), 2180 (C≡N), 1750, 1640 (C=O), 1580 cm^{-1} (C=C). − MS (70 eV, EI): *m*/*z* (%): 208 [M$^+$] (28).

General Procedure for the Synthesis of the Coordination Polymers 23 and 26: A solution of vinylogous amide ligand **21** (336 mg, 2 mmol) or **24** (442 mg, 2 mmol) in 40 mL methanol was added to a stirred solution of 1 mmol copper(II) acetate monohydrate in 50 mL methanol. After 1 h, the analytically pure precipitate was filtered off, dried in vacuo (oil pump), and crystallized.

1D-$^1_\infty$[CuL$^7_2$] (23): Yield: 397 mg (100%) as dark-green crystals from chloroform/diethyl ether; m.p. > 250 °C. − IR ($CHBr_3$): ṽ = 2960 (CH), 2190 (C≡N), 1625 (C=N), 1535 cm^{-1} (C=C). − MS (FAB): *m*/*z* (%): 628 [$Cu_2L_3{}^+$] (17), 460 [$Cu_2L_2{}^+$] (16), 398 [$CuL_2{}^+$] (11).

1D-$^1_\infty$[CuL$^8_2$] (26): Yield: 422 mg (97%) as turquoise-green crystals from chloroform/diethyl ether; m.p. > 250 °C (dec.). − IR ($CHBr_3$): ṽ = 2940, 2870 (CH), 2190 (C≡N), 1590 (C=N), 1490, 1480 (C=C). − MS (70 eV, EI): *m*/*z* (%): 485 [$CuL_2{}^+$] (56).

General Procedure for the Synthesis of the Coordination Polymers 29 and 32: A solution of vinylogous amide ligand **27** (336 mg, 2 mmol) or **30** (442 mg, 2 mmol) in 40 mL methanol was added to a stirred solution of copper(II) acetate monohydrate (200 mg, 1 mmol) in 50 mL methanol. Triethylamine (0.27 mL, 2 mmol) was then added and after 15 min the solvent was removed in vacuo. The residue was dissolved in 100 mL chloroform and the resulting solution was washed with water (3 × 50 mL) and dried with magnesium sulfate. The solvent was then removed and the product was crystallized. In the case of coordination polymer **29** it proved important to carry out all reaction steps at room temperature and to adhere strictly to the reaction time in order to prevent partial racemization.

(*P*)-/(*M*)-1D-$^1_\infty$[CuL$^{9(S)}_2$] (29): Yield: 380 mg (67%) as light-green crystals from chloroform/diethyl ether; m.p. 213 °C (dec.). − IR ($CHBr_3$): ṽ = 2980, 2880 (CH), 2200 (C≡N), 1730, (C=O), 1605 (C=N), 1510 cm^{-1} (C=C). − MS (FAB): *m*/*z* (%): 1510 [$Cu_4L_5{}^+$] (1), 1258 [$Cu_4L_4{}^+$] (25), 1195 [$Cu_3L_4{}^+$] (68), 944 [$Cu_3L_3{}^+$] (44), 881 [$Cu_2L_3{}^+$] (47), 630 [$Cu_2L_2{}^+$] (17), 566 [$CuL_2{}^+$] (100).

1D-$^1_\infty$[CuL$^{10(R)}$L$^{10(S)}$] (32): Yield: 233 mg (49%) as dark-green crystals from chloroform/diethyl ether; m.p. 209 °C (dec.). − IR ($CHBr_3$): ṽ = 2990, 2920 (CH), 2190 (C≡N), 1740 (C=O), 1590 (C=N), 1480 cm^{-1} (C=C). − MS (FAB): *m*/*z* (%): 1019 [$Cu_3L_4{}^+$] (6), 957 [$Cu_2L_4{}^+$] (0.3), 812 [$Cu_3L_3{}^+$] (1), 749 [$Cu_2L_3{}^+$] (15), 540 [$Cu_2L_2{}^+$] (6), 478 [$CuL_2{}^+$] (100).

Crystal Structure Determination of Compound 23: $C_{14}H_{14}CuN_4O_6$, M_r = 397.83, monoclinic space group $P2_1/n$, a = 674.53(8) pm, b = 898.31(24) pm, c = 1312.53(10) pm, β = 96.182(8)°, V = 0.7907(2) nm^3, Z = 2, ρ_{calcd} = 1.671 Mgm^{-3}, $F(000)$ = 406, λ =

71.073 pm, $T = 293(2)$ K, μ(Mo-K_α) = 1.422 mm^{-1}, crystal dimensions 0.40×0.040×0.30 mm, 5.5° ≤ 2Θ ≤ 52.6°; 1671 measured reflections, of which 1603 were independent (R_int = 0.0221) and were employed in the structure refinement (116 parameters, 0 restraints). The R values are $R1 = \Sigma\,|F_\mathrm{o} - F_\mathrm{c}|/|F_\mathrm{o}| = 0.0306$ [$I > 2\sigma(I)$] and $wR2 = [\Sigma W(F_\mathrm{o}^2 - F_\mathrm{c}^2)/\Sigma wF_\mathrm{o}^4]^{1/2} = 0.0897$ (all data); residual electron density (peak/hole): 391/−415 e/nm^3.

Crystal Structure Determination of Compound 26: $C_{26}H_{22}CuN_4O_2$, M_r = 486.05, monoclinic space group $P2_1/a$, a = 1054.0(2) pm, b = 1094.8(1) pm, c = 992.2(2) pm, β = 102.57(1)°, V = 1.1176(3) nm^3, Z = 2, ρ_calcd = 1.444 Mg m^{-3}, λ = 71.073 pm, μ(Mo-K_α) = 1.01 mm^{-1}, crystal dimensions 0.5×0.55×0.1 mm, θ range: 1.75° to 27.5°; 2563 measured reflections, of which 2316 were independent; data/parameter ratio 12.50. The final reliability indices based on 1888 reflections with $F > 3\sigma(F)$ were R = 0.039 and wR = 0.037 using the weighting scheme $w = 1/\sigma^2(F)$; min./max. residual electron density: 370/460 e/nm^3.

Crystal Structure Determination of Compound 29: $C_{24}H_{30}CuN_4O_8$, M_r = 566.06, monoclinic space group $P2_1$, a = 1241.2(3) pm, b = 1181.6(2) pm, c = 1905.7(4) pm, β = 105.28(3)°, V = 2.6962(9) nm^3, Z = 4, ρ_calcd = 1.394 Mg m^{-3}, $F(000)$ = 1180, λ = 71.073 pm, T = 293(2) K, μ(Mo-K_α) = 0.862 mm^{-1}, crystal dimensions 0.50×0.30×0.20 mm, 5.6° ≤ 2Θ ≤ 49.2°; 7900 measured reflections, of which 4791 were independent (R_int = 0.0406) and were employed in the structure refinement (667 parameters, 1 restraint). The R values are $R1$ = 0.0369 [$I > 2\sigma(I)$] and $wR2$ = 0.1039 (all data); residual electron density (peak/hole): 300/−424 e/nm^3.

Crystal Structure Determination of Compound 32: $C_{20}H_{22}CuN_4O_6$, M_r = 477.96, triclinic, space group $P\bar{1}$; a = 767.00(5) pm, b = 871.04(11) pm, c = 858.66(6) pm, α = 108.142(7)°, β = 94.301(6)°, γ = 103.008(8)°, V = 0.52459(8) nm^3, Z = 1, ρ_calcd = 1.513 Mg m^{-3}, $F(000)$ = 247, λ = 71.073 pm, T = 293(2) K, μ(Mo-K_α) = 1.086 mm^{-1}, crystal dimensions 0.30×0.30×0.10 mm, 5.1° ≤ 2Θ ≤ 48.1°; 1775 measured reflections, of which 1636 were independent (R_int = 0.0234) and were employed in the structure refinement (143 parameters, 0 restraints). The R values are $R1$ = 0.0373 [$I > 2\sigma(I)$] and $wR2$ = 0.1084 (all data); residual electron density (peak/hole): 643/−655 e/nm^3. − Crystallographic data for **23**, **29** and **32** were collected on Nonius CAD-MACH3 diffractometers equipped with graphite-monochromated Mo-K_α radiation by use of θ and ω scans. The structures were solved by direct methods (SHELX-86) and refined by full-matrix least-squares treatment against F^2 using the SHELXL-93 program system.[22] 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. − Crystallographic data for **26** were collected on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo-K_α radiation using the Wyckoff-scan technique. The structure was solved by direct phase determination and refined by full-matrix least-squares treatment using the SHELXTL-PLUS program system. The positions of the hydrogen atoms were included as a riding model without refinement and with fixed isotropic U. − Two-dimensional 2D-$^2_\infty$[CuL$^{11}_2$] **33** and 2D-$^2_\infty$[CuL$^{12}_2$] **34** were also obtained with ethyl (*Z*)-2-cyano-2-(pyrrolidine-2-ylidene)acetate (HL^{11}) and (*E*)-2-cyano-2-(oxazolidine-2-ylidene)-1-phenylethanone (HL^{12}). − Crystallographic data (excluding structure factors) for all structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-111706 (**23**), CCDC-111831 (**26**), CCDC-111702 (**29**), CCDC-111703 (**32**), CCDC-111704 (**33**), and CCDC-111705 (**34**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Volkswagen-Stiftung.

---

[1] J.-M. Lehn, *Supramolecular Chemistry − Concepts and Perspectives*, VCH, Weinheim, **1995**; D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1243−1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154−1196.

[2] S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558−1595; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1460−1494; R. Robson in: *Comprehensive Supramolecular Chemistry, Vol. 6* (Eds.: D. D. Manicol, F. Toda, R. Bishop), Pergamon, Oxford, **1996**, p. 733; C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton, A. H. White, *Angew. Chem.* **1998**, *110*, 970−972; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 920−922; M. J. Zaworotko, *Chem. Soc. Rev.* **1994**, 283−288; A. J. Blake, N. R. Champness, S. S. Chung, W.-S. Li, M. Schröder, *J. Chem. Soc.*, *Chem. Commun.* **1997**, 1005−1006; K. A. Hirsch, D. Venkataraman, S. R. Wilson, J. S. Moore, S. Lee, *J. Chem. Soc.*, *Chem. Commun.* **1995**, 2199−2200; L. Carlucci, G. Ciani, D. M. Proserpio, *J. Chem. Soc.*, *Chem. Commun.* **1994**, 2755−2756.

[3] R. W. Saalfrank, C.-J. Lurz, K. Schobert, O. Struck, E. Bill, A. X. Trautwein, *Angew. Chem.* **1991**, *103*, 1499−1501; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1494−1496; R. W. Saalfrank, O. Struck, K. Nunn, C.-J. Lurz, R. Harbig, K. Peters, H. G. von Schnering, E. Bill, A. X. Trautwein, *Chem. Ber.* **1992**, *125*, 2331−2335.

[4] R. W. Saalfrank, R. Harbig, O. Struck, E.-M. Peters, K. Peters, H. G. von Schnering, *Z. Naturforsch.* **1996**, *51b*, 399−408; R. W. Saalfrank, O. Struck, K. Peters, H. G. von Schnering, *Chem. Ber.* **1993**, *126*, 837−840. See also: R. W. Saalfrank, O. Struck, D. Danion, J. Hassa, L. Toupet, *Chem. Mater.* **1994**, *6*, 1432−1436.

[5] G. Denti, S. Serroni, S. Campagna, A. Juris, M. Ciano, V. Balzani in: *Perspectives in Coordination Chemistry* (Eds.: A. F. Williams, C. Floriani, A. E. Merbach), VCH, Weinheim, **1992**, p. 153.

[6] R. W. Saalfrank, R. Harbig, O. Struck, F. Hampel, E.-M. Peters, K. Peters, H. G. von Schnering, *Z. Naturforsch.* **1997**, *52b*, 125−134. See also: R. W. Saalfrank, D. Danion, F. Hampel, J. Hassa, O. Struck, L. Toupet, *Chem. Ber.* **1994**, *127*, 1283−1286; R. W. Saalfrank, K. Schobert, S. Trummer, A. Wolski, *Z. Naturforsch.* **1995**, *50b*, 642−648; M. J. Hannon, C. L. Painting, W. Errington, *J. Chem. Soc.*, *Chem. Commun.* **1997**, 1805−1806.

[7] M. Decker, Ph. D. Thesis, Univ. Erlangen-Nürnberg, Germany, **1997**.

[8] The diagram only shows the (*M*)-helix.

[9] R. W. Saalfrank, O. Struck, K. Peters, H. G. von Schnering, *Inorg. Chim. Acta* **1994**, *222*, 5−11.

[10] O. J. Gelling, F. van Bolhuis, B. L. Feringa, *J. Chem. Soc.*, *Chem. Commun.* **1991**, 917−919.

[11] D. A. Evans, K. A. Woerpel, M. J. Scott, *Angew. Chem.* **1992**, *104*, 439−441; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 430−433; J. F. Modder, G. van Koten, K. Vrieze, A. L. Spek, *Angew. Chem.* **1989**, *101*, 1723−1725; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1698−1700.

[12] R. W. Saalfrank, M. Decker, F. Hampel, K. Peters, H. G. von Schnering, *Chem. Ber./Recueil* **1997**, *130*, 1309−1313.

[13] In contrast to (*M*)-1D-$^1_\infty$[CuL$^{5(S)}_2$] **5**, (*P*)-1D-$^1_\infty$[CuL$^{6(R)}_2$] **6** and (*M*)-1D-$^1_\infty$[CuL$^{6(R)}_2$] **6** are generated in chloroform from the stable, less hindered, methanol precursors (*R*,*R*)-**19**(HOMe) and (*S*,*S*)-**19**(HOMe) by repetitive backside attack by one cyano group of a second molecule and loss of methanol according to an S_N2-type mechanism.[12]

[14] R. W. Saalfrank, O. Struck, M. G. Davidson, R. Snaith, *Chem. Ber.* **1994**, *127*, 2489−2492.

[15] The diagrams were created with the program MOLMOL and were rendered with the Persistence of Vision Raytracer, R. Koradi, M. Billeter, K. Wüthrich, *J. Mol. Graphics* **1996**, *14*, 51−55.

[16] The starting materials **21**, **24**, **27**, and **30** were prepared according to ref.[17]

[17] Y. Yamada, D. Milijkovic, P. Wehrli, B. Golding, P. Lölinger, R. Keese, K. Müller, A. Eschenmoser, *Angew. Chem.* **1969**, *81*, 301−306; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 343-348; H. Fritschi, U. Leutenegger, K. Siegmann, A. Pfaltz, W. Keller, C. Kratky, *Helv. Chim. Acta* **1988**, *71*, 1541−1552.

[18] G. M. Coppola, R. Damon, A. D. Kahle, M. J. Shapiro*, J. Org. Chem*. **1981**, *46*, 1221−1222.

[19] The helicity is defined with respect to the order of the copper(II) ions.

[20] B. F. Becker, H. P. Fritz, *Liebigs Ann. Chem.* **1976**, *6*, 1015−1022; B. Prager, P. Jacobson, *Beilsteins Handbuch der Organischen Chemie* **1921**, *H 3*, 658.

[21] G. M. Sheldrick, *SHELXL-93, Programm für die Kristallstrukturverfeinerung*/Program for Crystal Structure Refinement, Universität Göttingen, **1993**.

Received April 16, 1999
[I99136]