Spontaneous formation of a 1D-coordination polymer with helix structure starting from (*S*)-pyroglutamic acid and copper(II) acetate*

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Abstract

Reaction of a methanolic copper(II) acetate solution and (*S*)-methoxycarbonyl pyrrolidine (**6**) (HL^3) in the presence of triethylamine leads to a mixture of two charges of crystals that are easy to distinguish visually. According to X-ray crystal structure analyses the products are the pseudo dimeric molecular complex $[CuL^3_2]\cdot[CuL^4_2]$ (**12**) and the helical 1D-coordination polymer $([CuL^3_2]\cdot\frac{1}{2}Et_2O)_\infty$ (**3**). Prerequisite for the formation of the centrosymmetric complex **12** is the partial inversion of [(*S*),(*S*)-CuL^3_2] (**10**) (HL^3=**6**) to [(*R*),(*R*)-CuL^4_2] (**11**) (HL^4=**7**), induced by triethylamine. Complex **12** is formed via linking of monomers **10** and **11** across two of the four available MeO oxygens. The unit cell of the 1D-coordination polymer **3** is composed of two almost identical helix strands (Λ)-Cu(1)-**3** and (Δ)-Cu(2)-**3**. Each strand is generated by a set of very similar monomeric building blocks Cu(1)-**10** and Cu(2)-**10**. The structure data of (Λ)-Cu(1)-**3** and (Δ)-Cu(2)-**3**, reveal that each of the Cu(1) and Cu(2) atoms is linked across the N(28) atoms of only one neighbouring cyano group of the monomers **10**. The 1D-coordination polymer (Λ)-Cu(1)/(Δ)-Cu(2)-**3** cocrystallises with diethyl ether to form a clathrate.

Key words: Crystal structures; Copper complexes; Coordination polymer; Spontaneous self-organization

Introduction

Current research activities are focussed on the development of new strategies suitable for the generation of aggregates, bimolecular and up to nanostructural. As a rule, linkage of the individual building blocks occurs via hydrogen or metal bridges [1–3].

Recently we have shown that reaction of a methanolic copper(II) acetate solution and tetrazole **4** (HL^1) leads to the formation of the 3D-coordination polymer **1** of the general composition $[CuL^1_2]_\infty$ (HL^1=**4**, CuL^1_2=**8**) [4,5], whereas under exactly the same conditions pyrrolidine **5** (HL^2) forms the 2D-coordination polymer $[CuL^2_2]_\infty$ (**2**) (HL^2=**5**, CuL^2_2=**9**) [6].

A prerequisite for the formation of 3D/2D-coordination polymers **1** and **2** is the intermediate generation of the coordinatively unsaturated copper(II) building blocks **8** and **9**. The monomers **8** and **9** are bidentate. These coordinate through the two cyano groups, leading to linking of the monomers and to coordinative saturation at the copper(II) centres of **8** and **9** with formation of the corresponding three- and two-dimensional coordination polymers **1** and **2**.

During the formation of polymers **1** and **2**, the complexes **8** and **9** have a double function. They react as metals and, as well, as ligands [7]. The exact structures of **1** and **2** were established by X-ray crystallographic structure analyses [5,6]. In both polymers the copper(II) atoms are coordinated in the form of a slightly distorted tetragonal bipyramid.

Copper complexes with tetragonal-pyramidal structure, referring to **9** [6], are known. Hence, one expects building blocks that, in contrast to **8** and **9**, are sterically shielded at one side to couple only across one cyano group and therefore lead to polymers of reduced dimensionality. Additionally, the use of chiral, enantiomerically pure C_2-symmetric monomers CuL^3_2 (**10**) via asymmetric induction could make the enantiospecific synthesis of helical 1D-coordination polymers of type **3** possible [8] (Scheme 1).

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†Single-crystal X-ray structure analyses.

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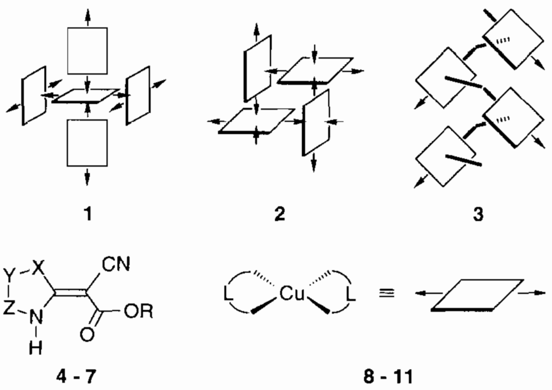

4 (HL^1): X = $NCMe_3$; Y-Z = N=N; R = CMe_3 **8** : L = L^1

5 (HL^2): X, Y, Z = CH_2; R = Me **9** : L = L^2

6 (HL^3): X, Y = CH_2; Z = (*S*)-$CHCO_2Me$; R = Me **10** : L = L^3

7 (HL^4): X, Y = CH_2; Z = (*R*)-$CHCO_2Me$; R = Me **11** : L = L^4

Scheme 1.

Hitherto, chiral, non-racemic, helical coordination polymers have only been described for Ag(I) and Cu(I) [9]. These polymers are generated via a fundamentally different route, compared to our strategy.

In this paper we report on the reaction of a methanolic copper(II) acetate solution and (*S*)-methoxycarbonyl pyrrolidine (**6**) (HL^3) in the presence of triethylamine. This leads to a mixture of products. By fractional recrystallisation we obtained two visually easily distinguishable charges of crystals. According to microanalyses, the products formed are compounds of the general stoichiometric composition $[CuL^3{}_2]_n$ and $([CuL^3{}_2]\cdot\frac{1}{2}Et_2O)_n$ ($HL^3 = \mathbf{6}$, $CuL^3{}_2 = \mathbf{10}$) (Scheme 1).

Experimental

General information

^1H NMR and ^{13}C NMR spectra were obtained on a Jeol JNM-GX-400 spectrometer with Me_4Si as internal standard and mass spectra on a Varian CH-48 instrument. Specific rotations were recorded on a Schmidt and Haensch polartronic E polarimeter. Melting points are not corrected.

Preparation of the ligand

The ligand (2*S*)-methyl 5-[(methyloxycarbonyl)-(cyano)methylidene]pyrrolidine-2-carboxylate (**6**) was prepared as described in the literature [10] from (2*S*)-methyl 5-ethoxy-3,4-dihydro-2*H*-pyrrol-2-carboxylate and methyl cyanoacetate, to give an 87% yield of colourless cubes by recrystallisation from CH_2Cl_2/Et_2O/hexane. The enantiomeric purity of (−)-**6** was checked by ^1H NMR with $Eu(hfc)_3$ in $CDCl_3$. M.p. 110–111 °C. ^1H NMR (400 MHz, $CDCl_3$): 2.23–2.32, 2.44–2.53 (2m, 2H, CH_2-CH), 2.94–3.09 (m, 2H, CH_2), 3.77, 3.80 (2s, 6H, $2OCH_3$), 4.60 (dd, $J = 8.8$, 5.5 Hz, 1H, CH), 9.17 (br s, 1H, NH). ^{13}C NMR (100.5 MHz, $CDCl_3$): 25.13 (CH_2–CH), 32.30 (CH_2), 51.55, 52.81 ($2OCH_3$), 62.03 (CH), 68.77 (=*C*CN), 117.86 (CN), 167.70, 170.62, 173.33 (2C=O, =C–N). MS (70 eV): 224 [M^+, 37%]. $[\alpha]_{578} = -20°$ ($c = 1.0$, $CHCl_3$, 23 °C). *Anal.* Calc. for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.39; N, 12.49. Found: C, 53.47; H, 5.40; N, 12.56%.

Preparation of the complexes

Pseudo dimer $[CuL^3{}_2]\cdot[CuL^4{}_2]$ *(12)*

To a solution of $Cu(OAc)_2\cdot H_2O$ (200 mg, 1 mmol) in 40 ml of methanol, racemic (+/−)-**6**/**7** (448 mg, 2 mmol) and triethylamine (0.27 ml, 2 mmol) were added. The green mixture was stirred at 23 °C for 10 min. The solvent was evaporated and the residue taken up in 100 ml of $CHCl_3$. The solution was washed with water (3×50 ml), dried ($MgSO_4$) and evaporated. The resulting crude product was crystallised from $CHCl_3/Et_2O$, to give a 96% yield of dark green needles. M.p. > 205 °C (dcc.). MS (70 eV): 572 [$M^+ + {}^{63}Cu$, 2%], 509 [M^+, 2%]. *Anal.* Calc. for $C_{20}H_{22}N_4O_8Cu$: C, 47.11; H, 4.35; N, 10.99. Found: C, 47.30; H, 4.35; N, 11.02%.

Helix coordination polymer $([CuL^3{}_2]\cdot\frac{1}{2}Et_2O)_\infty$ *(3)*

The helix polymer **3** was prepared like the pseudo dimeric complex **12** by using enantiomerically pure (−)-**6**. The product was crystallised from $CHCl_3/Et_2O$/petroleum ether at 4 °C, to give an 85% yield of green prisms. M.p. dec. MS (70 eV): 572 [$M^+ + {}^{63}Cu$, 1%], 509 [M^+, 3%]. $[\alpha]_{546} = 1100°$ ($c = 0.01$, $CHCl_3$, 23 °C). *Anal.* Calc. for $C_{20}H_{22}N_4O_8Cu\cdot 0.5(C_2H_5)_2O$: C, 48.31; H, 4.98; N, 10.24. Found: C, 47.28; H, 4.72; N, 10.44%.

*Crystallography**

X-ray data collection and processing of 12

The crystals of the Cu(II) complex **12** ($C_{20}H_{22}N_4O_8Cu$, $MW = 509.97$, monoclinic, $P2_1/n$, $a = 11.453(1)$, $b = 15.696(2)$, $c = 12.515(1)$ Å, $\beta = 100.15(1)°$, $V_c = 2252.7(4)$ Å^3, $Z = 4$, $D_c = 1.503$ Mg m^{-3}, $\mu = 1.04$ mm^{-1}, $F(000) = 1052$), were dark green prisms. X-ray diffraction data were obtained from a single crystal with appropriate dimensions (0.12×0.25×0.55 mm) at 294 K using a STOE/STADI4 diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The $\theta/2\theta$ scan technique was used with a θ_{max} value of 25.0°. Three reference reflections were measured once every hour. The intensity instability was <4%. The data reduction included corrections for background, Lorentz

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*See also 'Supplementary material'.

TABLE 1. Atomic parameters ($\times 10^4$) and equivalent isotropic[a] displacement coefficients U_{eq} ($\times 10^{-1}$) (pm^2) for the non-hydrogen atoms in the pseudo dimeric complex **12** with e.s.d.s in parentheses

	x	y	z	U_{eq}[a]
Cu	−927(1)	−933(1)	−1998(1)	42(1)
O(2)	−310(2)	176(2)	−1423(2)	46(1)
C(3)	−776(4)	682(3)	−862(4)	45(2)
C(4)	−1933(4)	604(3)	−624(4)	43(2)
C(5)	−2696(4)	−57(3)	−1015(4)	40(2)
C(6)	−3930(4)	−111(3)	−779(4)	51(2)
C(7)	−4444(4)	−866(4)	−1392(5)	107(3)
C(8)	−3483(4)	−1256(3)	−1912(4)	58(2)
N(9)	−2445(3)	−695(2)	−1610(3)	46(1)
O(10)	−1232(2)	−2163(2)	−1975(2)	49(1)
C(11)	−613(4)	−2744(3)	−2232(3)	43(2)
C(12)	441(4)	−2656(3)	−2661(3)	40(2)
C(13)	909(4)	−1849(3)	−2835(3)	41(2)
C(14)	2052(4)	−1745(3)	−3281(4)	49(2)
C(15)	2098(3)	−793(3)	−3510(4)	51(2)
C(16)	1189(3)	−404(3)	−2876(4)	43(2)
N(17)	469(3)	−1118(2)	−2613(3)	39(1)
O(18)	−184(3)	1376(2)	−452(3)	58(1)
C(19)	922(4)	1553(3)	−809(4)	59(2)
C(20)	−2359(4)	1247(3)	26(4)	54(2)
N(21)	−2734(4)	1731(3)	548(4)	88(2)
C(22)	−3859(5)	−1348(4)	−3103(5)	89(3)
O(22)	−4753(5)	−1644(5)	−3471(5)	263(5)
O(23)	−3129(3)	−1089(3)	−3688(3)	80(2)
C(24)	−3419(5)	−1189(4)	−4837(4)	113(4)
O(25)	−920(3)	−3554(2)	−2097(3)	58(1)
C(26)	−1959(4)	−3691(3)	−1621(4)	76(2)
C(27)	1039(4)	−3385(3)	−2943(4)	47(2)
N(28)	1529(3)	−3964(3)	−3194(3)	67(2)
C(29)	402(4)	255(3)	−3517(4)	42(2)
O(29)	−631(3)	172(2)	−3888(3)	59(1)
O(30)	1018(3)	958(2)	−3614(3)	57(1)
C(31)	397(5)	1647(3)	−4207(4)	79(3)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \alpha_i \alpha_j$.

as well as polarisation effects, and for absorption via Ψ-scan. The cell parameters were refined against θ values of 170 centred reflections with $2\theta > 25°$. A total of 5136 reflections was collected with $h \leqslant 13$, $k \leqslant |18|$, $l \leqslant |15|$, of which 3918 were unique reflections.

*Structure determination and refinement of **12***

The structure was solved by direct phase determination and refined by full-matrix least-squares treatment using the Siemens SHELXTL PLUS program system. The positions of the hydrogen atoms are of riding model and they were included without refinement and with fixed isotropic U. The number of refined parameters was 299, goodness of fit = 2.42. The final reliability indices based on 2790 reflections with $F > 3\sigma(F)$ were $R = 0.057$ and $R_w = 0.038$, using the weighting $w = 1/\sigma^2(F)$. The maximum and minimum $\Delta\rho$ values in the final difference map were 0.63 and −0.59 e Å^{-3}, respectively. All calculations were carried out on a personal computer. Atomic parameters and equivalent isotropic displacement coefficients are given in Table 1.

*X-ray data collection and processing of **3***

The crystals of the Cu(II) complex **3** (2 $C_{20}H_{22}N_4O_8Cu + C_4H_{10}O$, $MW = 1094.05$, orthorhombic, $P2_12_12_1$, $a = 19.525(3)$, $b = 21.611(4)$, $c = 12.102(2)$ Å, $V_c = 5106(1)$ Å^3, $Z = 4$, $D_c = 1.423$ Mg m^{-3}, $\mu = 0.91$ mm^{-1}, $F(000) = 2242$) were pale green needles. X-ray diffraction data were obtained from a single crystal with appropriate dimensions (0.4×0.45×3.85 mm) at 294 K using a Siemens R3m/V diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The Wyckoff scan technique was used with a θ_{max} value of 27.5°. All 100 reflections three reference reflections were measured. The crystal decomposed during the measurement down to a final reflecting power of about 70%. The data reduction included corrections for background, decay, Lorentz as well as polarisation effects, and for absorption via Ψ-scan. The cell parameters were determined by a LSQ refinement of 22 centred reflections with $21 < 2\theta < 24°$. A total of 6491 reflections was collected with $h \leqslant 25$, $k \leqslant 28$, $l \leqslant 15$, of which 6456 were unique reflections.

*Structure determination and refinement of **3***

The structure was solved by direct phase determination and refined by full-matrix least-squares treatment using the Siemens SHELXTL PLUS program system. The positions of the hydrogen atoms are of riding model and they were included without refinement and with fixed isotropic U. The number of refined parameters was 641, goodness of fit = 2.66. The final reliability indices based on 5634 reflections with $F > 3\sigma(F)$ were $R = 0.055$ and $R_w = 0.051$, using the weighting $w = 1/\sigma^2(F)$. The maximum and minimum $\Delta\rho$ values in the final difference map were 0.97 and −0.52 e Å^{-3}, respectively. All calculations were carried out on a personal computer. Atomic parameters and equivalent isotropic displacement coefficients are given in Table 2.

Results and discussion

According to an X-ray crystal structure analysis the byproduct $[CuL^3{}_2]_n$ of the reaction of a methanolic copper(II) acetate solution and (*S*)-methoxycarbonyl pyrrolidine (**6**) (HL^3) in the presence of triethylamine represents a pseudo dimeric molecular complex with $n = 2$ and the exact composition $[CuL^3{}_2]\cdot[CuL^4{}_2]$. A prerequisite of the formation of the centrosymmetric pseudo dimer $[CuL^3{}_2]\cdot[Cu(a)L^4{}_2]$ (**12**) (Fig. 1) is the partial inversion of [(*S*),(*S*)-$CuL^3{}_2$] (**10**) to [(*R*),(*R*)-

TABLE 2. Atomic parameters ($\times 10^4$) and equivalent isotropic[a] displacement coefficients U_{eq} ($\times 10^{-1}$) (pm^2) for the non-hydrogen atoms in the helix coordination polymer **3** with e.s.d.s in parentheses

	x	y	z	U_{eq}[a]
Cu(1)	6799(1)	9241(1)	8634(1)	44(1)
O(2)	5849(2)	9287(2)	9150(3)	53(1)
C(3)	5633(3)	9268(3)	10117(5)	47(2)
C(4)	6044(3)	9169(3)	11057(4)	51(2)
C(5)	6747(3)	9064(3)	11021(4)	47(2)
C(6)	7152(3)	8948(3)	12051(4)	52(2)
C(7)	7884(3)	8978(3)	11672(4)	54(2)
C(8)	7830(3)	8915(3)	10388(4)	49(2)
N(9)	7121(2)	9063(2)	10127(3)	45(2)
O(10)	7748(2)	9242(2)	8090(3)	55(1)
C(11)	7962(3)	9304(3)	7110(5)	48(2)
C(12)	7537(3)	9371(3)	6161(4)	47(2)
C(13)	6823(3)	9316(3)	6206(4)	44(2)
C(14)	6402(3)	9279(3)	5174(5)	61(2)
C(15)	5692(4)	9279(5)	5584(5)	92(3)
C(16)	5740(3)	9165(4)	6842(5)	55(2)
N(17)	6462(2)	9285(3)	7106(3)	49(2)
O(18)	4966(2)	9334(3)	10329(3)	71(2)
C(19)	4499(3)	9412(4)	9420(6)	85(3)
C(20)	5719(3)	9153(4)	12119(5)	73(3)
N(21)	5462(3)	9157(5)	12972(5)	110(3)
C(22)	8016(3)	8272(3)	9980(5)	55(2)
O(22)	7652(3)	7936(2)	9499(5)	81(2)
O(23)	8671(2)	8145(3)	10226(4)	84(2)
C(24)	8946(5)	7592(5)	9882(9)	135(5)
O(25)	8636(2)	9287(3)	6903(3)	67(2)
C(26)	9103(3)	9203(5)	7813(6)	93(3)
C(27)	7863(3)	9460(3)	5110(5)	53(2)
N(28)	8094(3)	9552(3)	4242(4)	73(2)
C(29)	5533(4)	8528(4)	7195(6)	76(3)
O(29)	4936(3)	8355(3)	7152(7)	132(4)
O(30)	6024(3)	8190(2)	7602(5)	81(2)
C(31)	5864(6)	7602(4)	7947(10)	131(6)
Cu(2)	1734(1)	9049(1)	4056(1)	50(1)
O(2)	1972(2)	8866(2)	2487(3)	57(1)
C(3)	1560(3)	8960(3)	1682(5)	57(2)
C(4)	849(3)	9021(3)	1740(5)	58(2)
C(5)	492(3)	8947(3)	2727(5)	55(2)
C(6)	−264(3)	8891(4)	2778(7)	76(3)
C(7)	−410(3)	8650(5)	3923(7)	111(4)
C(8)	255(3)	8766(4)	4552(6)	71(3)
N(9)	769(2)	8915(2)	3715(4)	55(2)
O(10)	1459(2)	9319(2)	5559(3)	59(1)
C(11)	1845(3)	9478(3)	6339(4)	49(2)
C(12)	2559(3)	9479(2)	6342(4)	44(2)
C(13)	2949(3)	9284(3)	5425(4)	43(2)
C(14)	3702(3)	9288(3)	5424(5)	63(2)
C(15)	3904(3)	8929(4)	4444(6)	72(3)
C(16)	3254(3)	8892(3)	3748(5)	54(2)
N(17)	2697(2)	9079(2)	4486(4)	47(1)
O(18)	1838(3)	8989(2)	656(3)	74(2)
C(19)	2575(4)	8895(4)	551(6)	89(3)
C(20)	482(4)	9093(4)	729(6)	75(3)
N(21)	160(4)	9151(4)	−43(6)	115(3)
C(22)	438(4)	8204(4)	5155(7)	85(3)
O(22)	933(4)	7877(3)	4922(6)	133(3)
O(23)	40(3)	8065(3)	5962(5)	118(3)
C(24)	128(7)	7485(6)	6488(10)	222(9)
O(25)	1547(2)	9661(2)	7295(3)	64(2)
C(26)	812(3)	9644(4)	7382(6)	90(3)
C(27)	2893(3)	9646(3)	7339(5)	49(2)
N(28)	3172(3)	9798(3)	8140(4)	67(2)
C(29)	3169(4)	8246(3)	3293(6)	68(2)
O(29)	3512(3)	8067(3)	2528(5)	114(3)
O(30)	2725(3)	7913(2)	3821(4)	81(2)
C(31)	2640(6)	7296(4)	3429(9)	133(5)
O(32)	2263(8)	7625(5)	7697(11)	206(8)
C(33)	1929(11)	7924(8)	7882(13)	237(13)
C(34)	2699(9)	7722(8)	6674(13)	242(10)
C(35)	1373(8)	7239(7)	8847(10)	208(9)
C(36)	3340(7)	7801(8)	6749(14)	347(15)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \alpha_i \alpha_j$.

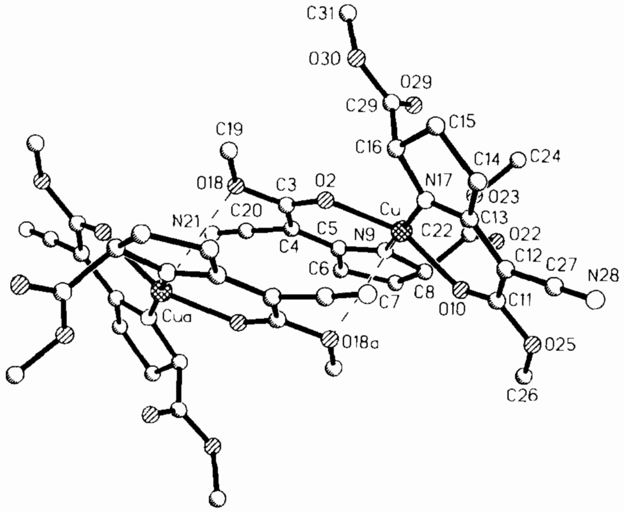

Fig. 1. Structure of *meso*-pseudodimer $[CuL^3_2]\cdot[Cu(a)L^4_2]$ (**12**) in the crystal (H atoms omitted). Selected bond lengths (pm) and angles (°): Cu–O(2) 196.8(3), Cu–N(9) 192.2(4), Cu–O(18a) 318.2, Cu(a)–O(18) 318.2; O(2)–Cu–N(9) 91.0(1), O(2)–Cu–O(10) 156.7(1), N(9)–Cu–O(10) 91.0(1), N(9)–Cu–N(17) 170.9(1).

$CuL^4_2]$ (**11**), induced by triethylamine*. Complex **12** is formed via linking of monomers **10** and **11** across two of the four available MeO oxygens [11]. The central Cu/Cu(a) atoms in *meso*-**12** are identical and nearly tetragonal-pyramidally coordinated. The planes of the two ligands L^3 ($HL^3 = $ **6**) coordinated to the Cu centre (the same is true for Cu(a)) are twisted by an angle of 24.9° (torsion angle: angle between the perpendiculars

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*The degree of racemisation depends on the reaction time. If this time is below 10 min, the formation of *meso*-**12** can almost be suppressed. Starting from racemic HL^3(**6**)/HL^4(**7**), complex **12** is formed nearly quantitatively. Surprisingly no centrosymmetric $[(S),(R)\text{-}CuL^3L^4]$ is formed besides C_2-symmetric $[(S),(S)\text{-}CuL^3_2]$ and $[(R),(R)\text{-}CuL^4_2]$.

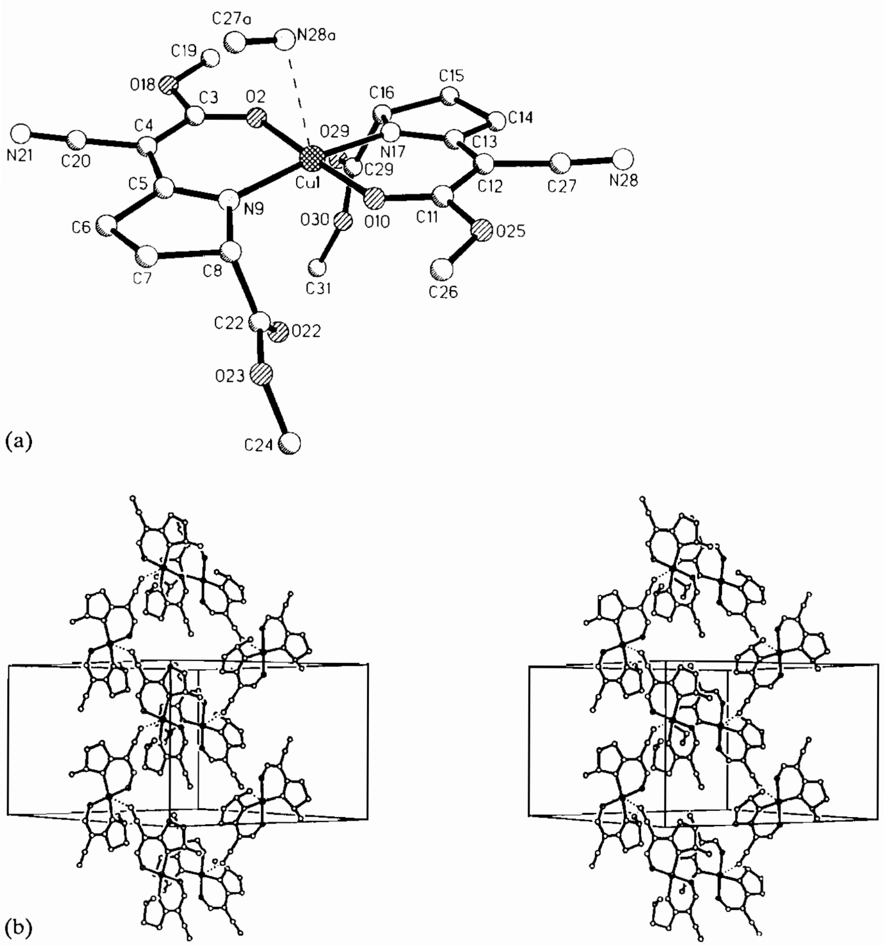


Fig. 2. (a) Structure of monomer Cu(1)-**10** (Cu(2)-**10** differs only slightly from Cu(1)-**10** and is not shown) in the crystal (H atoms omitted). Selected bond lengths (pm) and angles (°): Cu(1)–O(2) 196.1(4), Cu(1)–O(10) 196.6(4), Cu(1)–N(9) 195.1(4), Cu(1)–N(17) 196.6(4), Cu(1)–N(28a) 270.5; O(10)–Cu(1)–N(17) 90.0(2), O(2)–Cu(1)–O(10) 176.9(2), N(9)–Cu(1)–N(28a) 85.1, C(4)–Cu(1)–N(28a) 80.7, C(27a)–N(28a)–Cu(1) 116.1. (b) Stereoview (without $(H_5C_2)_2O$) of crystal packing of (Λ)-Cu(1)-**3** (left strand) and (Δ)-Cu(2)-**3** (right strand). For reasons of clarity methoxycarbonyl groups are represented only by their carbonyl carbon atoms, H atoms are omitted.

of the planes O(2)–Cu–N(9) and O(10)–Cu–N(17)). The Cu–O(18a) and Cu(a)–O(18) distances are both 318.2 pm.

In contrast to **12**, $([CuL^3_2]\cdot\frac{1}{2}Et_2O)_n$ represents a polymer with $n=\infty$. The formation of the 1D-coordination polymer **3** is understandable if one assumes the intermediate formation of a coordinatively unsaturated C_2-symmetric copper(II) building block [(*S*),(*S*)-CuL^3_2] (**10**), which is sterically shielded at one side by two methoxy carbonyl groups. Therefore, contrary to **8** and **9**, coordination of **10** with only one cyano group is possible. This leads to tetragonal-pyramidal coordination at the copper(II) centres with formation of 1D-$[CuL^3_2]_\infty$ (**3**) (Scheme 2).

The exact structure of **3** was determined by X-ray crystallographic structure analysis. According to this analysis the crystal is composed of two almost identical helix strands (Λ)-Cu(1)-**3** and (Δ)-Cu(2)-**3** (central helices). Each strand is generated by a set of identical monomeric building blocks Cu(1)-**10** and Cu(2)-**10**, respectively, which differ only slightly in bond lengths and bond angles (Fig. 2).

The available structure data of (Λ)-Cu(1)-**3** and (Δ)-Cu(2)-**3**, reveal that each of the Cu(1) and Cu(2) atoms is linked across the N(28) atom of only one neighbouring cyano group of the monomers **10**. The central Cu atoms in (Λ)-Cu(1)-**3** and (Δ)-Cu(2)-**3** are almost tetragonal-pyramidally coordinated, with the planes of the two ligands L^3 ($HL^3=$ **6**) in (Λ)-Cu(1)-**3** twisted against each other to form an angle of 9.0° (torsion angle: angle between the perpendiculars of the planes O(2)–Cu(1)–N(9) and O(10)–Cu(1)–N(17)). The distances Cu(1)–N(28a) and Cu(2)–N(28b) are 270.5 pm for (Λ)-Cu(1)-**3** and 272.4 pm for (Δ)-Cu(2)-**3**. Contrary to 3D- and 2D-polymers **1** and **2**, the monomers **10** in the helix polymer **3** are not positioned perpendicular to each other. The bond angles of C(27a)–N(28a)–Cu(1) and C(27b)–N(28b)–Cu(2) in **3** have been

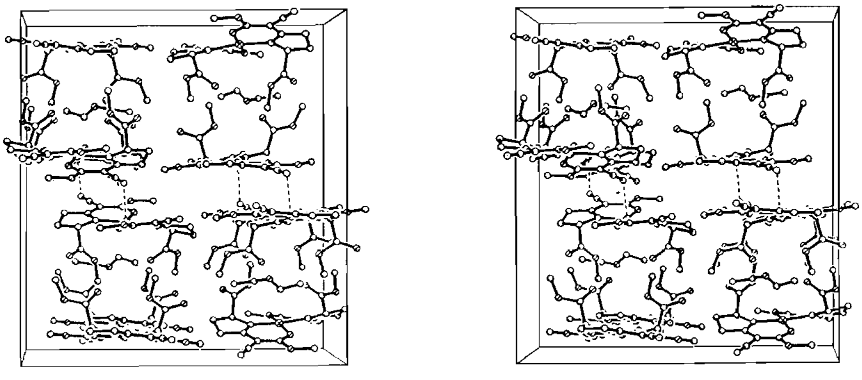
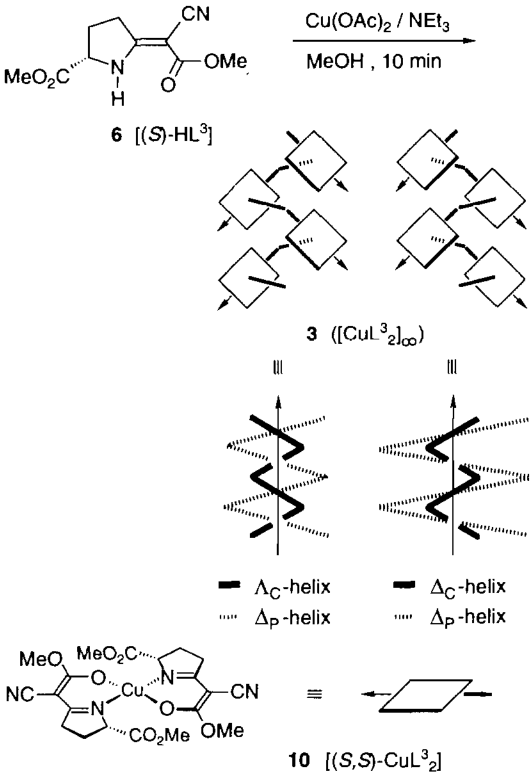


Fig. 3. Stereoview of the unit cell of the clathrate $([\mathrm{CuL}^3_2]\cdot\frac{1}{2}\mathrm{Et_2O})_\infty$ (**3**) (view along the crystallographic 2_1 axis; H atoms omitted).



Scheme 2.

found to be 116.1 and 128.9°, respectively (compared with almost 180° in **1** and **2**).

Strictly speaking, the helix strands (Λ)-Cu(1)-**3** and (Δ)-Cu(2)-**3** (central helices) generate a pair of diastereoisomers composed of enantiomerically pure, C_1-symmetric (*S*)-L^3 ligands (HL^3 = **6**) and copper(II) ions, crystallising in the same unit cell. Only very few compounds are known with structural isomers next to each other in the same crystal [12].

More detailed studies show that the stereogenic centres (or the pyrrolidine ring centres) of monomers **10** in **3** for (Λ)-Cu(1)-**3** and (Δ)-Cu(2)-**3** describe peripheric (Δ)-helices (pitch angle: (Δ)-peripheric-helix-Cu(1)-**3** > (Δ)-peripheric-helix-Cu(2)-**3**; pitch: (Δ)-peripheric-helix-Cu(1)-**3** ≈ (Δ)-peripheric-helix-Cu(2)-**3**) (Scheme 2).

The 1D-coordination polymer (Λ)-Cu(1)/(Δ)-Cu(2)-**3** cocrystallises with diethyl ether to form a clathrate [13] (stoichiometry: host/guest (**10**/Et$_2$O) = 2/1). The guest molecules are surrounded by methoxycarbonyl groups in the interior of tubes consisting of (Λ)-Cu(1)/(Δ)-Cu(2)-**3** pairs (Fig. 3).

All the more surprising, therefore, is the high degree of symmetry obtained by linking of the C_2-symmetric monomers **10**. Spontaneous self-organisation [1–6] yields chiral one-dimensional coordination polymers with central (Λ)- and (Δ)-strands in the unit cell.

Supplementary material

Further details concerning the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein Leopoldshafen (Germany), on quoting the depository number CSD-56972, the names of the authors and the journal citation.

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