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Synthesis and Structural Characterization of Copper(II) Coordination Polymers from Ethyl Aminomethylenecyanoacetate Derivatives

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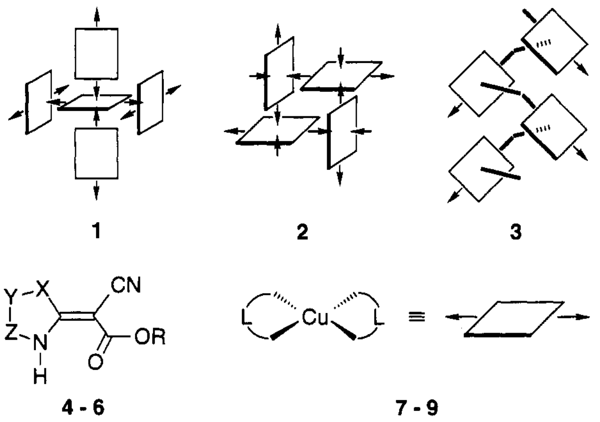
The reaction of copper(II) acetate with ethyl aminomethylenecyanoacetate derivatives **10** (H_2L^4) or **13** (H_2L^5) provides thermally highly stable products, that are insoluble in noncoordinating solvents. Single-crystal X-ray diffraction of the copper(II) chelates **11** ($[CuL^4]_\infty$) and **14** ($[CuL^5]_\infty$) established unequivocally the structures of the coordination polymers. Initially, coordinatively unsaturated copper(II) intermediates **12** and **15** are formed, disposing two CN donor groups in the equatorial plane of the chelates. Thus the bidentate building blocks **12** and **15** undergo *spontaneous self-organization*, by performing coordination of CN groups on the axial positions of the intermediary chelates, leading to coordinative saturation of the copper(II) centers. The supramolecular 2D geometry of the coordination polymers **11** and **14** depends basically on the lateral groups of the chelate ligands.

Introduction

Biology provides striking illustrations of thermodynamically stable architectures, such as the tobacco mosaic virus, the DNA and numerous protein complexes, generated via self-assembly.[1] Though the conceptual origins of self-assembly are rooted in biology, self-assembly is by no means restricted to biology.[2] In synthetic chemistry self-assembly leads basically to discrete nanoscale molecular devices and has therefore been proposed as a strategy for the development of new materials.

In the context of our research interests in organized entities, we reported on the formation of the neutral coordination polymers 3D-**1**, 2D-**2**, and helical 1D-**3**. They are generated by *spontaneous self-organization* from the tridentate ligands **4–6** and copper(II) acetate via the coordinatively unsaturated bidentate building blocks **7–9**[3–5] (Scheme 1).

Scheme 1



4 (HL^1): X = $NCMe_3$; Y-Z = N=N; R = CMe_3 **7** : L = L^1

5 (HL^2): X, Y, Z = CH_2; R = Me **8** : L = L^2

6 (HL^3): X, Y = CH_2; Z = (*S*)-$CHCO_2Me$; R = Me **9** : L = L^3

To contribute additional material to the chemistry of solid state, we applied our strategy for the development of coordination polymers **1–3** to tetradentate ethyl aminomethylenecyanoacetate derivatives **10** and **13** as chelate ligands. Having basically been studied by Jäger, however with different objectives,[6,7] these ligands were supposed to provide coordination polymers of variable architectures. The ligands **10** and **13** structurally closely resemble the

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Table 1. Important Bond Lengths of 11 ($[CuL^4]_\infty$) (in pm)[a]

Cu–O(1)	197.1(3)	Cu–N(1)	194.2(3)	Cu–N(3a)	278.4(5)
Cu–O(2)	197.9(3)	Cu–N(2)	192.9(3)	Cu–N(4a)	256.7(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2. Important Bond Angles of 11 ($[CuL^4]_\infty$) (in deg)[a]

O(1)–Cu–O(2)	91.8(1)	O(2)–Cu–N(3a)	103.2(2)
O(1)–Cu–N(2)	169.8(1)	N(2)–Cu–N(4a)	90.6(2)
O(2)–Cu–N(1)	174.3(1)	N(2)–Cu–N(3a)	86.1(2)
O(2)–Cu–N(2)	92.3(1)	N(3A)–Cu–N(4a)	173.6(3)
N(1)–Cu–N(2)	84.0(1)	O(1)–Cu–N(3a)	83.9(2)
O(1)–Cu–N(4a)	99.4(2)	N(1)–Cu–N(3a)	80.9(2)
O(2)–Cu–N(4a)	108.1(2)	N(1)–Cu–N(4a)	81.1(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3. Atomic Parameters and Equivalent Isotropic Displacement Coefficients B for the Non-Hydrogen Atoms in Polymer 11, Esds in Parentheses

atom	x	y	z	B (Å^2)
Cu	0.51394(5)	0.17546(4)	0.27105(4)	2.949(9)
O(1)	0.6619(3)	0.1007(2)	0.3796(2)	2.92(6)
O(2)	0.4518(3)	0.2346(2)	0.3933(2)	3.28(6)
O(3)	0.3489(3)	0.3542(2)	0.4676(2)	4.51(7)
O(4)	0.8055(3)	−0.0302(2)	0.4327(2)	3.73(6)
N(1)	0.5711(3)	0.1305(2)	0.1438(2)	2.56(7)
N(2)	0.3558(3)	0.2250(2)	0.1563(3)	2.72(7)
N(3)	0.1133(4)	0.4867(3)	0.2646(4)	5.9(1)
N(4)	0.8700(4)	−0.1509(3)	0.2194(3)	5.02(9)
C(1)	0.4910(4)	0.1781(3)	0.0386(3)	3.23(9)
C(2)	0.3479(4)	0.1866(3)	0.0443(3)	3.37(9)
C(3)	0.2710(4)	0.2922(3)	0.1708(3)	2.81(8)
C(4)	0.2741(4)	0.3353(3)	0.2746(3)	2.91(8)
C(5)	0.3646(4)	0.3036(3)	0.3791(3)	3.18(9)
C(6)	0.7266(4)	0.0291(3)	0.3515(3)	2.67(8)
C(7)	0.7297(4)	0.0039(3)	0.2427(3)	2.55(8)
C(8)	0.6543(4)	0.0566(3)	0.1445(3)	2.57(8)
C(9)	0.1844(4)	0.4189(4)	0.2725(4)	4.0(1)
C(10)	0.8086(4)	−0.0814(3)	0.2304(3)	3.41(9)
C(11)	0.4457(5)	0.3356(4)	0.5776(4)	4.5(1)
C(12)	0.4080(5)	0.2471(5)	0.6334(5)	5.9(1)
C(13)	0.8074(6)	−0.0119(4)	0.5473(4)	5.2(1)
C(14)	0.8823(6)	−0.0959(4)	0.6178(4)	5.6(1)

tetrazolyl enol **4** or the pyrrolinyl enols **5** and **6**. In contrast to **4–6**, the two [N,O] donor units in **10** and **13** are connected by a lateral group [$-(CH_2)_n-$; **10**: $n = 2$, **13**: $n = 3$]. The alkyl chains allow to exert a crucial influence on the geometry of the intermediary chelates and thus on the ensuing coordination polymers **11** and **14**.

Experimental Section

General measurements were made as follows: Melting points (uncorrected): Kofler table (Type WMB, Reichert). IR spectra: Perkin-Elmer 1420. ^{1}H NMR: Bruker, AC 300P (300 MHz, internal TMS). ^{13}C NMR: Bruker, AC 300P (75.5 MHz, TMS int.). Mass spectra: Varian MAT 311 (direct emission, 70 eV). The elementary analyses have been carried out at the "Laboratoire de Microanalyse du CNRS/Lyon".

Table 4. Important Bond Lengths of 14 ($[CuL^5]_\infty$) (in pm)[a]

Cu–O(1)	197.4(2)	Cu–N(1)	194.9(3)	Cu–N(3a)	251.3(3)
Cu–O(2)	198.7(2)	Cu–N(2)	195.0(3)	Cu–N(4a)	308.6(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 5. Important Bond Angles of 14 ($[CuL^5]_\infty$) (in deg)

O(1)–Cu–O(2)	86.8(1)	N(1)–Cu–N(2)	92.1(1)
O(1)–Cu–N(1)	92.3(1)	O(2)–Cu–N(2)	92.3(1)
O(1)–Cu–N(2)	157.7(1)	O(2)–Cu–N(1)	170.3(1)
O(2)–Cu–N(4a)	108.1(2)	O(2)–Cu–N(3a)	81.7(2)
N(1)–Cu–N(4a)	81.1(2)	N(2)–Cu–N(4a)	80.5(3)
N(1)–Cu–N(3a)	89.2(2)	N(2)–Cu–N(3a)	98.3(2)
O(1)–Cu–N(3a)	86.8(2)	N(3A)–Cu–N(4a)	170.2(4)
O(1)–Cu–N(4a)	78.6(2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 6. Atomic Parameters and Equivalent Isotropic Displacement Coefficients B for the Non-Hydrogen Atoms in Polymer 14, Esds in Parentheses

atom	x	y	z	B (Å^2)
Cu	0.98370(4)	0.18685(4)	0.73681(3)	2.898(8)
O(1)	0.8619(2)	0.1014(2)	0.6240(2)	2.98(5)
O(2)	1.0367(2)	0.2478(2)	0.6072(2)	3.08(5)
O(3)	0.7357(3)	−0.0356(2)	0.5657(2)	4.14(6)
O(4)	1.1338(2)	0.3670(2)	0.5258(2)	3.95(6)
N(1)	0.9089(2)	0.1447(2)	0.8582(2)	2.42(6)
N(2)	1.1448(2)	0.2248(2)	0.8441(2)	2.43(6)
N(3)	0.6283(3)	−0.1417(3)	0.7721(3)	4.38(8)
N(4)	1.3935(3)	0.4703(3)	0.7147(3)	5.55(9)
C(1)	0.8289(3)	0.0701(3)	0.8500(3)	2.40(7)
C(2)	0.7763(3)	0.0092(3)	0.7537(3)	2.52(7)
C(3)	0.7970(3)	0.0297(3)	0.6465(3)	2.61(7)
C(4)	1.2282(3)	0.2858(3)	0.8207(3)	2.54(7)
C(5)	1.2204(3)	0.3350(3)	0.7156(3)	2.62(7)
C(6)	1.1243(3)	0.3124(3)	0.6164(3)	2.76(7)
C(7)	0.9405(3)	0.2067(3)	0.9620(3)	3.71(9)
C(8)	1.0771(4)	0.2136(4)	1.0201(3)	5.1(1)
C(9)	1.1722(3)	0.1813(3)	0.9580(3)	3.36(8)
C(10)	0.7519(6)	−0.0256(4)	0.4536(4)	7.4(1)
C(11)	0.6508(7)	−0.0728(5)	0.3714(4)	8.6(2)
C(12)	1.0374(4)	0.3525(4)	0.4200(3)	4.4(1)
C(13)	1.0644(4)	0.2642(4)	0.3563(4)	5.4(1)
C(14)	0.6943(3)	−0.0745(3)	0.7635(3)	3.07(8)
C(15)	1.3150(3)	0.4097(3)	0.7126(3)	3.44(8)

Ethyl Aminomethylenecyanoacetate Derivatives ($H_2L^{4,5}$). General Procedure. A solution of 12 mmol of the corresponding diamine in 50 mL of dichloromethane was added dropwise to a solution of 4.06 g (24 mmol) of ethyl ethoxymethylenecyanoacetate[8] in 50 mL of dichloromethane. After 1 h the addition of the diamine was complete, and the yellow solution was stirred for 3 h at 20 °C. The product precipitated at −20 °C on addition of 15 mL of hexane. After filtration and washing with diethyl ether, the product was recrystallized from 40 mL of ethanol/diethyl ether (4:1). NMR studies showed that the reaction yielded a mixture of E/Z stereoisomers. They underwent rapid rearrangement during chelate formation and were used without further separation.

Ethyl Ethylenediamine-*N,N'*-dimethylenecyanoacetate 10 (H_2L^4). According to the general procedure, **10** (H_2L^4) was obtained by reaction of 4.06 g (24 mmol) of ethyl ethoxymethylenecyanoacetate with 0.72 g (12 mmol) of ethylenediamine. Yield: 3.12 g (85%), *three E/Z isomers*, white needles, mp: 146 °C. IR (Nujol) $\tilde{\nu}$ = 3280 (NH), 2180 ($C\equiv N$), 1670 ($C{=}O$), 1605, 1600 cm^{-1} ($C{=}C$). ^{1}H NMR (300 MHz, DMSO-d_6) δ = 1.14 (m, 6 H, 2 CH_3), 3.40 (m, 4 H, 2 CH_2), 4.15 (m, 4 H, 2 OCH_2), 7.61–7.88 (m, 2 H, 2 $=CH$), 9.05 (br s, 2 H, NH) ppm. ^{13}C NMR (75.5 MHz, DMSO-d_6), occasional overlap of signals: δ = 10.29, 10.37 (2 CH_3), 44.88, 45.07 (2 NCH_2), 55.68 (2 OCH_2), 64.98, 65.15, 65.26, 65.97 (2 $=C(CN)$), 111.72, 111.75, 115.05, 115.10 (2 CN), 156.29, 156.58 (2 $=CH$), 161.83, 162.40 (2 $C{=}O$) ppm. EI-MS (70 eV) m/z (%) 306 (39.0) [M^+]. Anal. Calcd for $C_{14}H_{18}N_4O_4$ (306.3): C, 54.90; H, 5.92; N 18.29. Found: C, 55.05; H, 5.79; N, 18.50.

Ethyl 1,3-Diaminopropane-*N,N'*-dimethylenecyanoacetate 13 (H_2L^5). According to the general procedure, **13** (H_2L^5) was obtained by reaction of 4.06 g (24 mmol) of ethyl ethoxymethylenecyanoacetate with 0.89 g (12 mmol) of 1,3-diaminopropane. Yield: 3.31 g (86%), three *E/Z isomers,* white needles, mp 115 °C. IR (Nujol): $\tilde{\nu}$ = 3285 (NH), 2200 ($C\equiv N$), 1690, 1680 ($C{=}O$), 1620 cm^{-1} ($C{=}C$). ^{1}H NMR (300 MHz, DMSO-d_6) δ =

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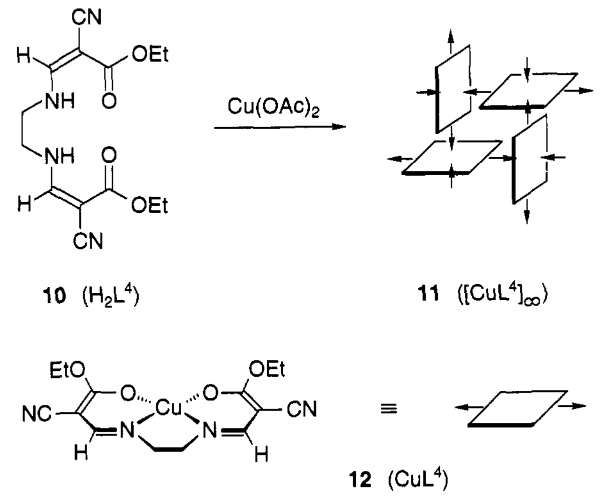
Scheme 2



1.19 (m, 6 H, 2 CH_3), 1.80 (m, 2 H, CH_2), 3.34 (m, 4 H, 2 NCH_2), 4.11 (m, 4 H, 2 OCH_2), 7.75, 7.95 (d, br s, 2 H, 2 =CH), 8.64, 9.12 (br s, m, 2 H, 2 NH) ppm. ^{13}C NMR (75.5 MHz, DMSO-d_6), occasional overlap of signals: δ = 10.28, 10.37 (2 CH_3), 26.88, 27.12, 27.23 (CH_2), 41.81, 41.93, 42.09, 42.14 (2 NCH_2), 55.55, 55.58, 55.93 (2 OCH_2), 64.65, 64.74, 65.41, 65.50 (2 =C(CN)), 112.87, 114.30, 115.21 (2 CN), 150.90, 155.72, 156.09, 156.13 (2 =CH), 161.12, 161.95, 162.57, 162.62 (2 C=O) ppm. EI-MS (70 eV) *m/z* (%) 320 (11.2) [M^+]. Anal. Calcd for $C_{15}H_{20}N_4O_4$ (320.3): C, 56.24; H, 6.29; N, 17.49. Found: C, 56.24; H, 6.37; N, 17.49.

Copper(II) Chelates of Ethyl Aminomethylenecyanoacetate Ligands ($[CuL^{4,5}]_\infty$). General Procedure. A solution of 1 mmol of the corresponding ethyl aminomethylenecyanoacetate **10** (H_2L^4) or **13** (H_2L^5) in 40 mL of dry methanol was added to a solution of 0.20 g (1 mmol) of $Cu(OAc)_2{\cdot}H_2O$ in 20 mL of dry methanol. After this stirred for 3 h, the complex was precipitated and filtered, washed with diethyl ether, and dried under reduced pressure.

[Diethyl 3,3′-(1,2-Ethanediyldinitrilo)bis[2-cyanopropanoato]-copper(II)] (11, $[CuL^4]_\infty$). According to the general procedure, **11** ($[CuL^4]_\infty$) was obtained by reaction of 0.31 g (1 mmol) of **10** (H_2L^4) with 0.20 g (1 mmol) of $Cu(OAc)_2{\cdot}H_2O$. Yield: 0.28 g (76%), blue crystals, mp >260 °C (lit. 245 °C).[6] IR (Nujol): ñ = 2195 (C≡N), 1610 (C=N), 1520, 1510 cm^{-1} (C=C). EI-MS (70 eV): *m/z* (%) = 367 (80.0) [M^+]. Anal. Calcd for $C_{14}H_{16}N_4O_4Cu$ (367.9): C, 45.71; H, 4.38; N, 15.23; Cu, 17.27. Found: C, 45.58; H, 4.39; N, 15.44; Cu, 17.52.

X-ray Structure Analysis of 11.[9] Dark blue parallelepipeds from methanol/ether/pentane. M = 367.85 ($CuO_4N_4C_{14}H_{16}$), monoclinic, $P2_1/n$, a = 10.305(7), b = 13.375(5), c = 12.447(7) Å, β = 107.49(5)′, V = 1636(1) Å^3, Z = 4, d_{calcd} = 1.52 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ = 13.80 cm^{-1}, F(000) = 756, T = 294 K, final R = 0.032 for 1822 observations.

The sample (0.40 × 0.40 × 0.50 mm) was studied on an automatic diffractometer CAD4 ENRAF-NONIUS by using graphite-monochromatized Mo Kα radiation. The cell parameters were obtained by fitting a set of 25 high-θ reflections. The data collection ($2\theta_{max}$ = 50°, scan $\omega/2\theta$ = 1/1, t_{max} = 60 s, range *hkl*: h = 0–12, k = 0–15, l = −14 to 14) intensity controls without appreciable decay (0.1%) gave 3155 reflections from which 1822 were independent (R_{int} = 0.015) with $I > 4\sigma(I)$.

After Lorentz and polarization corrections the structure was solved using direct methods which revealed the Cu and the two N and O atoms. The remaining non-hydrogen atoms of the structure were found after successive scale factor refinements and difference Fourier syntheses. After isotropic (R = 0.098), then anisotropic refinement (R = 0.049), the hydrogen atoms were found from a difference Fourier map (between 0.92 and 0.27 e Å^{-3}). The whole structure was refined by the full-matrix least-squares technique (use of F magnitude; x, y, z, β_{ij} for Cu, C, O, and N atoms and x, y, z for H atoms; 257 variables and 1822 observations; $w = 1/\sigma(F_0)^2 = [\sigma^2(I) + (0.04F_0^2)^2]^{-1/2}$) with the resulting R = 0.032, R_w = 0.037, and S_w = 1.21 (residual $\Delta\rho \leq 0.29$ e Å^{-3}). Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (1974). All the calculations were performed on a Digital MicroVAX 3100 computer with the MOLEN package (Enraf-Nonius, 1990, Tables 1–3).

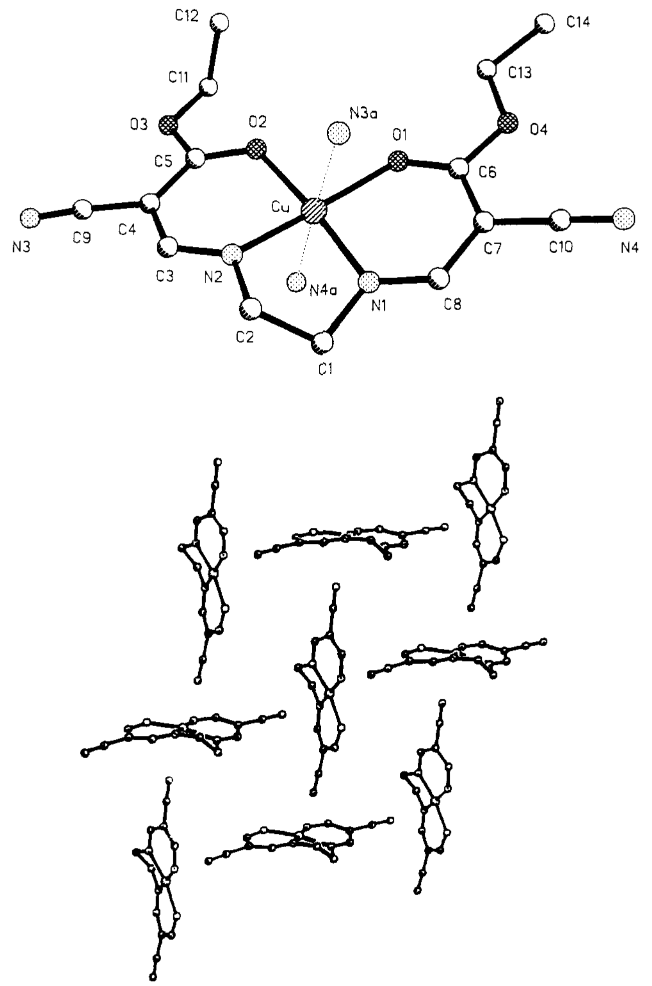


Figure 1. Top: structure of the monomeric unit of 2D-polymer **11** in the crystal (H atoms omitted). Bottom: crystal packing of 2D-polymer **11** ($[CuL^4]_\infty$, H atoms omitted).

[Diethyl 3,3′-(1,3-Propanediyldinitrilo)bis[2-cyanopropanoato]copper(II)] (14, $[CuL^5]_\infty$). According to the general procedure, **14** ($[CuL^5]_\infty$) was obtained by reaction of 0.32 g (1 mmol) of **13** (H_2L^5) with 0.20 g (1 mmol) of $Cu(OAc)_2{\cdot}H_2O$. Yield: 0.21 g (55%), green crystals, mp > 260 °C. IR (Nujol) ñ = 2200 (C≡N), 1620 (C=N), 1530, 1505 cm^{-1} (C=C). EI-MS (70 eV) *m/z* (%): 381 (100) [M^+]. Anal. Calcd for $C_{15}H_{18}N_4O_4Cu$ (381.9): C, 47.18; H, 4.75; N, 14.67; Cu, 16.65. Found: C, 46.94; H, 4.82; N, 14.47; Cu, 16.42.

X-ray Structure Analysis of 14.[9] Dark green parallelepipeds from methanol/ether/pentane. M = 381.90 ($CuO_4N_4C_{15}H_{18}$), monoclinic, $P2_1/n$, a = 10.844(3), b = 12.911(8), c = 12.233(9) Å, β = 105.38(7)°, V = 1651(1) Å^3, Z = 4, d_{calcd} = 1.54 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ = 13.49 cm^{-1}, F(000) = 788, T = 294 K, final R = 0.029 for 1854 observations.

The sample (0.15 × 0.25 × 0.30 mm) was studied on an automatic diffractometer CAD4 ENRAF-NONIUS by using graphite-monochromatized Mo Kα radiation. The cell parameters were obtained by fitting a set of 25 high-θ reflections. The

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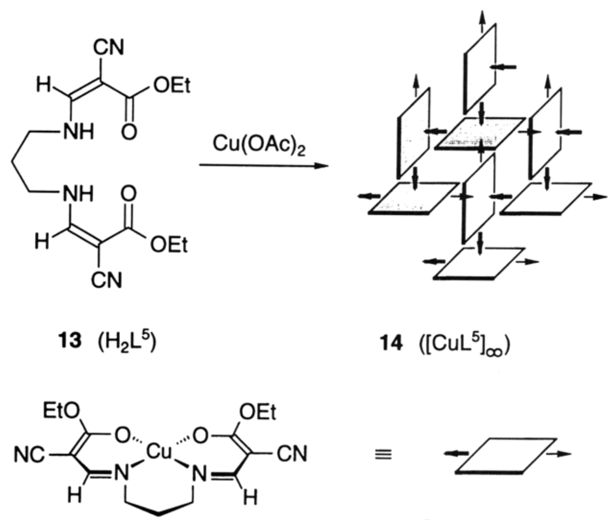
[9] The X-ray structure analyses were carried out by Dr. L. Toupet of the "Groupe Matière Condensée et Materiaux" URA 804 CNRS, Université de Rennes I, Bat. 11B Campus de Beaulieu, 35042 Rennes Cedex. Further details concerning the X-ray structure analyses of 11 and 14 can be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ, UK, on quoting the full journal citation.

Scheme 3



13 (H_2L^5)

14 ($[CuL^5]_\infty$)

15 (CuL^5)

data collection ($2\theta_{max} = 50°$, scan $\omega/2\theta = 1/1$, $t_{max} = 60$ s, range hkl: $h = 0$–12, $k = 0$–14, $l = -15$ to 15) intensity controls without appreciable decay (0.1%) gave 3209 reflections from which 1854 were independent ($R_{int} = 0.011$) with $I > 3\sigma(I)$.

After Lorentz and polarization corrections, the structure was solved using direct methods which revealed most of the non-hydrogen atoms of the molecule, the remaining ones being found after successive scale factor refinements and difference Fourier syntheses. After isotropic ($R = 0.095$) and then anisotropic refinement ($R = 0.058$), the hydrogen atoms were found from a difference Fourier map (between 0.41 and 0.16 e Å^{-3}). The whole structure was refined by the full-matrix least-squares technique (use of F magnitude; x, y, z, β_{ij} for Cu, C, O, and N atoms and x, y, z for H atoms; 272 variables and 1854 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o{}^2)^2]^{-1/2}$) with the resulting $R = 0.032$, $R_w = 0.029$, and $S_w = 1.11$ (residual $\Delta\rho \leq 0.27$ e Å^{-3}). Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (1974). All the calculations were performed on a Digital MicroVAX 3100 computer with the MOLEN package (Enraf-Nonius, 1990, Tables 4–6).

Results and Discussion

2D-Copper(II) Coordination Polymer 11. The product obtained by the reaction of copper(II) acetate with ethyl ethylenediamine-*N*,*N*′-dimethylenecyanoacetate **10** (H_2L^4) is almost completely insoluble in noncoordinating solvents and is thermally highly stable. According to the microanalysis, the general composition of product **11** corresponds to $[CuL^4]_\infty$.

The X-ray structure analysis of the copper (II) complex **11** ($[CuL^4]_\infty$) clearly proves a well-ordered, infinite two-dimensional architecture. The formation of coordination polymer **11** becomes understandable, if one assumes initial double deprotonation of **10**, which provides intermediate formation of planar copper(II) chelate **12** (CuL^4) by means of the $(2N,2O)^{2-}$ donor set. Chelate **12** may be considered as a bidentate monomeric building block, that looks for coordinative saturation. Basically, this can be achieved through intermolecular linkage of equatorial CN groups to the free axial positions in **12**. As a result a given monomer **12** (CuL^4) is surrounded by a total of four monomeric building blocks. Two of them are perpendicularly coordinated on the axial positions (Cu←NC acceptor interaction) and two are docking on the two equatorial CN groups (CN→Cu donor interaction) of the central monomer.

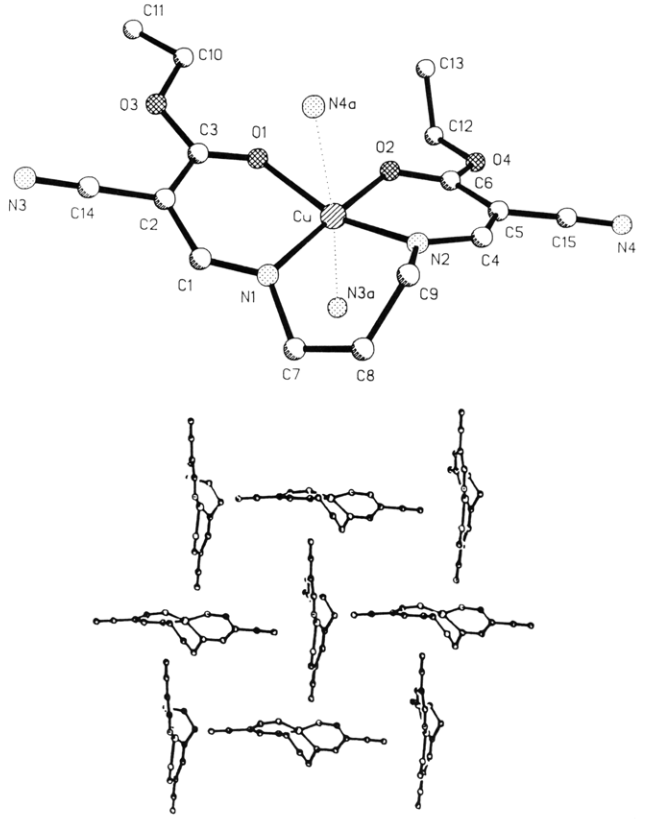


Figure 2. Top: structure of the monomeric unit of polymer **14** in the crystal (H atoms omitted). Bottom: crystal packing of polymer **14** ($[CuL^5]_\infty$, H atoms omitted).

This is another example of a monomer **12** (CuL^4) serving as a bidentate ligand and also as an unsaturated metal center ready for coordination.[10] The use of preprogrammed monomers like **12** is a prerequisite for *spontaneous self-organization* giving rise to highly ordered 2D-coordination polymers as **11** ($[CuL^4]_\infty$, Scheme 2).

According to the X-ray structure analysis, the central copper atom of **11** ($[CuL^4]_\infty$) is coordinated in a slightly distorted tetragonal bipyramid (Figure 1). The bond distances of the central copper atom to the enolato oxygens and imino nitrogens, that set up the tetragonal plane, are 197.1 [Cu–O(1)], 197.9 [Cu–O(2)], 194.2 [Cu–N(1)], and 192.9 pm [Cu–N(2)]. The angles of the equatorially coordinated enolato oxygen or imino nitrogen atoms to the axially coordinated cyano nitrogens do not deviate more than 10° from orthogonality.

The bond distances of the central copper atom to the axially coordinated CN nitrogens N(3a) and N(4a) correspond to 278.4 and 256.7 pm, the angle N(3a)–Cu–N(4a) is 173.6°. The inequality of the two Cu–NC distances is due to a minor twist [torsional angle: N(1)–C(1)–C(2)–N(2) 45.1°] within the lateral group [$-(CH_2)_2-$].

Copper(II) Coordination Polymer 14. Similar, as described for **11** ($[CuL^4]_\infty$), reaction of copper(II) acetate with ethyl 1,3-diaminopropane-*N*,*N*′-dimethylenecyanoacetate **13** (H_2L^5) leads to a crystalline product **14** ($[CuL^5]_\infty$). The formation of coordination polymer **14** becomes understandable, if one assumes initial double deprotonation of **13**, which provides intermediate formation of a distorted copper(II) complex **15** ($[CuL^5]$). Chelate **15** may

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[10] Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. Denti, G.; Serroni, S.; Campagna, S.; Juris, A.; Ciano, M.; Balzani, V. *Perspectives in Coordination Chemistry*; Williams, A. F., Floriani, C., Merbach, A. E., Eds.; VCH: Weinheim, 1992, p 153.

be considered as a bidentate monomeric building block, that looks for coordinative saturation. Basically, **15** ([CuL^5]) undergoes polymerization as reported for **12** ([CuL^4], Scheme 3).

In contrast to polymer **11**, the tetragonal bipyramidal coordination of the central copper atom of **14** ([CuL^5]$_\infty$) is significantly distorted, as has been shown by X-ray analysis (Figure 2). This is the result of the homologated lateral group [$-(CH_2)_3-$], compared to [$-(CH_2)_2-$], leading to a considerable folding of monomer **15** ([CuL^5]).

The atoms O(1), O(2), and N(1) are situated in a plane together with the copper center, whereas N(2) is markedly out of plane [angle: O(1)–Cu–N(2) 157.7°]. The peripheric propylene chain is equally out of plane, thus rendering one side of the monomer less accessible for axial CN coordination to the metal center.

The bond distances of the copper atom to the axially coordinated CN nitrogens N(3a) and N(4a) are 251.3 and 308.6 pm [angle: N(3a)–Cu–N(4a) 170.2°]. Given the substantial inequality of 57 pm between the Cu–NC–bond distances, an ideal 2D structure as seen for **11** ([CuL^4]$_\infty$) is not possible for **14** ([CuL^5]$_\infty$). The structure of **14** formally consists of interconnected stairlike strings [distance between strings: Cu–N(4a) 308.6 pm]. The monomers of the strings are tightly linked [distance between monomers: Cu–N(3a) 251.3 pm].

The structure of coordination polymer **14** ([CuL^5]$_\infty$) is somewhere in between a 2D and a 1D architecture due to the distortion caused by the lateral group [$-(CH_2)_3-$].

In conclusion we find, that the *spontaneous polymerization* of the coordinatively unsaturated chelate intermediates **12** ([CuL^4]) and **15** ([CuL^5]) is governed by their free cyano groups. The final topology of the supramolecular architecture is determined by the length of the lateral group [$-(CH_2)_n-$].

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Supplementary Material Available: Structures of 11 and 14 and tables and thermal parameters, bond distances, and angles (18 pages). Ordering information is given on any current masthead page.