Coordination Polymers, VI[1]

Neutral 1D-Coordination Polymers from Ethyl (Aminomethylene)cyanoacetate Derivatives and Copper(II) Acetate by Spontaneous Self-Organization

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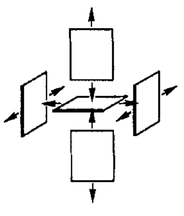
Reaction of a solution of copper(II) acetate in methanol with ethyl (aminomethylene)cyanoacetate derivatives **10** (H_2L^4) or **13** (H_2L^5) yields the corresponding 1D-coordination polymers **11** ($[CuL^4]_\infty$) and **14** ($[CuL^5]_\infty$), respectively. The products are insoluble in non-coordinating solvents and thermally highly stable. The structures of **11** and **14** have been established by X-ray diffraction. The one-dimensional coordination polymers **11** and **14** have different geometries, depending on the lateral group of the ligands.

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**[2–4]. They are generated by *spontaneous self-organization*[5] from the tridentate ligands **4**–**6** and copper(II) acetate via the coordinatively unsaturated bidentate building blocks **7**–**9**.



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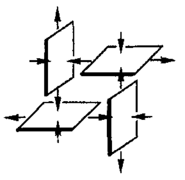

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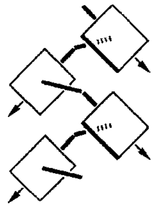

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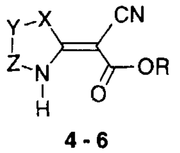
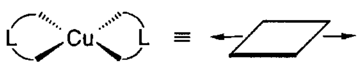


4 - 6



7 - 9

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

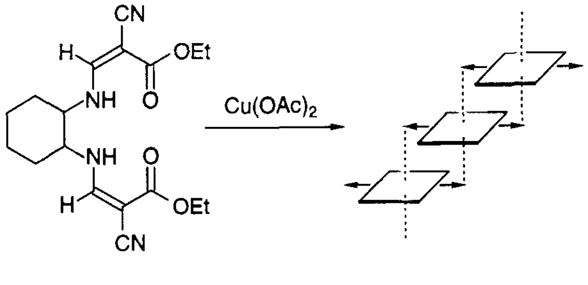
In order to contribute additional material to the chemistry of the organic solid state, we applied our strategy for the development of coordination polymers **1**–**3** to hexadentate ethyl (aminomethylene)cyanoacetate derivatives **10** and **13** as chelate ligands. Having basically been studied by Jäger, however with different objectives[6], these ligands were supposed to provide coordination polymers of variable architectures. The ligands **10** and **13** structurally closely resemble 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 [**10**: -(C_6H_{10})-, **13**: -$(CH_2)_4$-]. The alkyl chains exert a crucial influence on the geometry of the chelates and thus on the ensuing coordination polymers **11** and **14**.

Results and Discussion

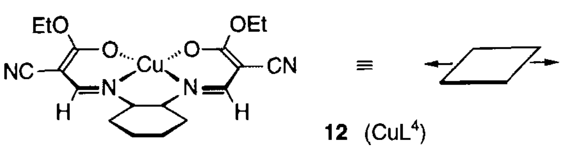
The product obtained by the reaction of copper(II) acetate with diethyl *trans*-1,2-cyclohexanediylbis(aminomethylene)bis(cyanocetate) (**10**) (H_2L^4) is almost completely insoluble in non-coordinating solvents and is thermally highly stable. According to the microanalysis, the general composition of product **11** corresponds to $[CuL^4]_\infty$.

X-Ray structure analyses of the copper(II) complexes **1** and **2** clearly prove the presence of well-ordered infinite three- and two-dimensional architectures[2,3]. The formation of the coordination polymers 3D-**1** and 2D-**2** is understandable, if one assumes initial deprotonation of **4** and **5**, which provides planar copper(II) chelates **7** and **8** as intermediates. Chelates **7** and **8** may be considered as bidentate monomeric building blocks that require coordinative saturation. Basically, this can be achieved by intermolecular linkage of equatorial CN groups to the free axial positions in **7** and **8**. As a result, in **1** and **2** a given monomer **7** or **8** is surrounded by a total of four monomeric building blocks. Two of them are coordinated perpendicularly to the axial positions (Cu ← NC acceptor interaction), and two are located on the two equatorial CN groups (CN → Cu donor interaction) of the central monomer.

In contrast to 3D-**1** and 2D-**2**, the coordinatively unsaturated building blocks **12** generate a one-dimensional stair-like polymer **11**. In **11**, the monomers **12** are not arranged perpendicularly as **7** and **8** in **1** and **2** but parallel, with the equatorial cyano groups coordinated axially to the copper centers.



10 (H_2L^4) **11** ($[CuL^4]_\infty$)



12 (CuL^4)

According to an X-ray structure analysis of **11** the copper(II) center is coordinated as a slightly distorted tetragonal bipyramide (Figure 1). The bond distances of the central copper atom to the axially coordinated CN nitrogens N(3a) and N(4a) are 303.8 and 316 pm.

Reaction of diethyl 1,4-butanediylbis(aminomethylene)bis(cyanoacetate) (**13**) (H_2L^5) with copper(II) acetate yields a green copper(II) chelate, which is almost insoluble in non-coordinating solvents. According to the microanalysis, the general composition of **14** corresponds to $[CuL^5]_\infty$.

The formation of the 1D-coordination polymer **14** is understandable, if one assumes initial double deprotonation of **13** (H_2L^5) leading to intermediate formation of trigonal-pyramidal copper(II) chelate **15**. The formally bidentate chelate **15** may be considered as a monodentate monomeric building block that requires coordinative saturation. Basically, this can be achieved by intermolecular linkage of one CN group to the free coordination site of **15**.

According to an X-ray structure analysis of **14** the copper atom is trigonal-bipyramidally coordinated (Figures 2 and 3). The trigonal plane is set up by O(1), N(2), and N(3a) [angles: O(1)–Cu–N(3a) 107.3, O(1)–Cu–N(2) 106.5, and N(2)–Cu–N(3a) 146.1°]. The axial positions in **14** are occupied by N(1) and O(2) [angle: N(1)–Cu–O(2) 174.4°, and N(1)–Cu–N(2) 93.2°].

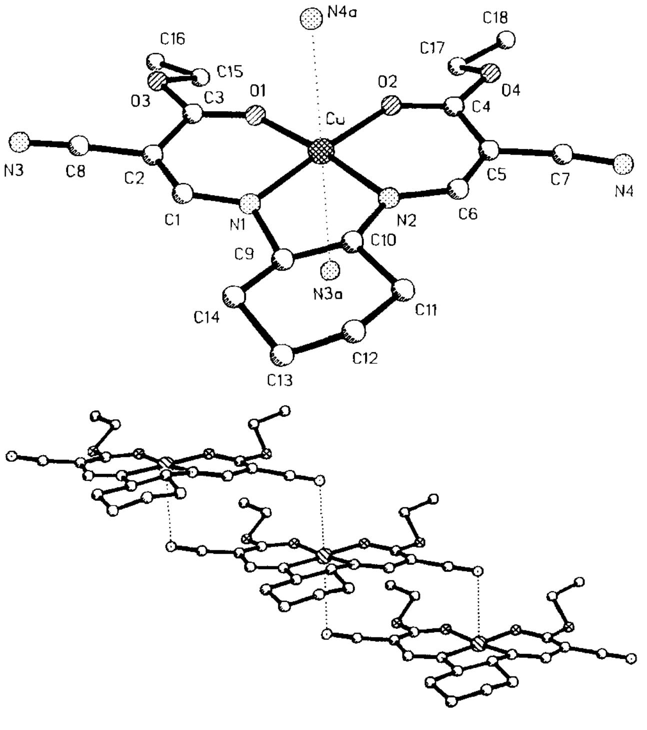
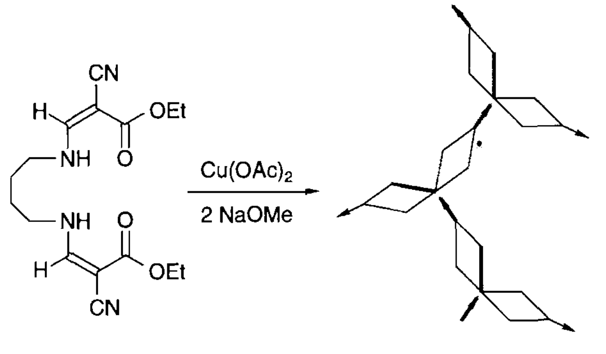
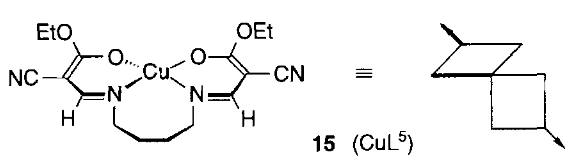


Figure 1. Top: Structure of the monomeric unit of coordination polymer **11** in the crystal (H atoms have been omitted for clarity); selected bond lengths [pm] and angles [°]: Cu–O(1) 189.1(6), Cu–N(1) 189.4(7), Cu–N(3a) 303.8(2), Cu–N(4a) 316; O(1)–Cu–O(2) 89.5(3), O(1)–Cu–N(1) 90.3(3), O(1)–Cu–N(2) 174.9(3), O(2)–Cu–N(4a) 92.6, O(2)–Cu–N(3a) 90.9, N(3a)–Cu–N(4a) 174.8. – Bottom: Crystal packing of 1D-coordination polymer **11**



13 (H_2L^5) **14** ($[CuL^5]_\infty$)



15 (CuL^5)

The Cu–N(3a) distance of 204.1 pm is rather short compared with Cu–N(1) 196.0, Cu–N(2) 198.2, Cu–O(1) 216.5, and Cu–O(2) 195.2 pm. In contrast to hexacoordinated **1** and **2**, in **14** copper is only pentacoordinated. This leaves one cyano group uncoordinated and as in **3** leads to reduction of dimensionality resulting in a zig-zag 1D-structure for **14**.

Monomers **12** and **15** are further examples for compounds serving as ligands and also having unsaturated metal centers susceptible to coordination[7]. The use of preprogrammed monomers like **12** and **15** is a prerequisite for *spontaneous self-organization* giving rise to highly ordered

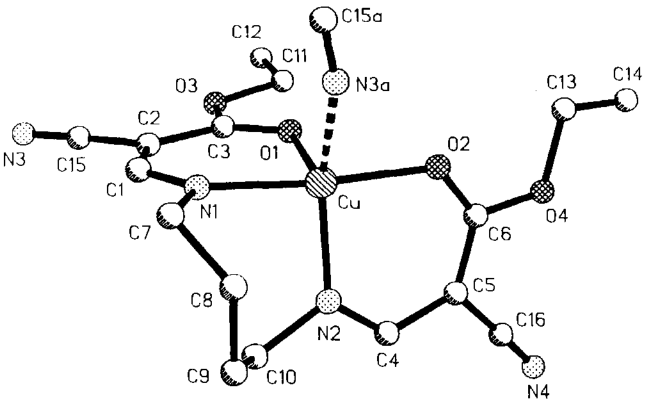


Figure 2. Structure of the monomeric unit of coordination polymer **14** in the crystal (H atoms have been omitted for clarity); selected bond lengths [pm] and angles [°]: Cu–O(1) 216.5(4), Cu–N(1) 196.0(4), Cu–N(3a) 204.1; O(1)–Cu–O(2) 87.1(2), O(2)–Cu–N(1) 174.4(2), O(1)–Cu–N(3a) 107.3, O(2)–Cu–N(3a) 88.6, N(1)–Cu–N(3a) 88.9, N(2)–Cu–N(3a) 146.1

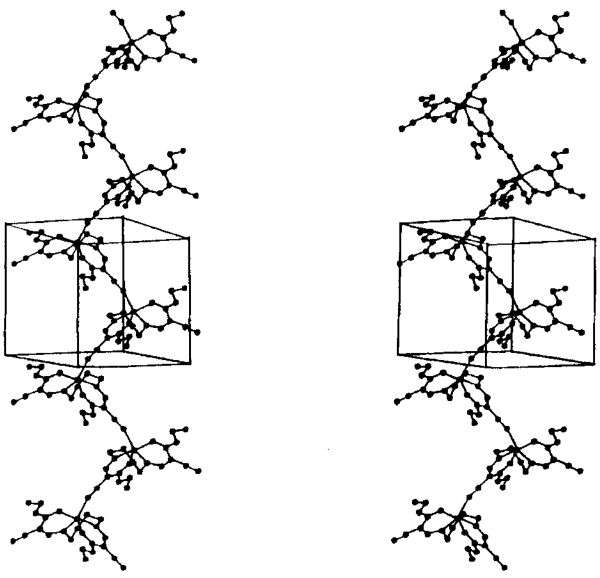


Figure 3. Stereoview of the crystal packing of 1D-coordination polymer **14**

1D-coordination polymers as **11** ($[CuL^4]_\infty$) and **14** ($[CuL^5]_\infty$).

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Experimental

Melting points (uncorrected): Kofler table (Type WMB, Reichert). – IR: Perkin-Elmer 1420. – ^{1}H NMR: Bruker AC 300P (300 MHz, TMS int.). – ^{13}C NMR: Bruker AC 300P (75.5 MHz, TMS int.). – MS: Varian-MAT 311 (direct emission, 70 eV). – Elementary analyses: Laboratoire de Microanalyse du CNRS/Lyon.

A) *Ethyl (Aminomethylene)cyanoacetate Derivatives* **10** *and* **13**. – *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 (ethoxymethylene)cyanoacetate[8] in 50 ml of dichloromethane. After 1 h the addition 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 of the product with diethyl ether, it 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.

Diethyl trans-1,2-Cyclohexanediylbis(aminomethylene)bis(cyanoacetate) (**10**): According to the general procedure **10** was obtained by reaction of 4.06 g (24 mmol) of ethyl (ethoxymethylene)cyanoacetate with 1.37 g (12 mmol) of 1,2-*trans*-diaminocyclohexane. Yield: 3.38 g (78%) of white needles, three *E*/*Z* isomers, m.p. 167°C. – IR (Nujol): $\tilde{\nu}$ = 3230, 3200 cm^{-1} (NH), 2200 (C≡N), 1670 (C=O), 1620, 1600 (C=C). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.11 (m, 8H, 2 CH$_3$ and CH$_2$), 1.30–2.01 (m, 6H, 3 CH$_2$), 3.30 (br. s, 2H, 2 NCH), 4.05 (m, 4H, 2 OCH$_2$), 7.54, 7.78 (2 d, 2H, 2 =CH), 8.50, 8.90 (br. s, m, 2H, 2 NH). – ^{13}C NMR (75.5 MHz, [D$_6$]DMSO), occasional overlap of signals: δ = 10.19, 10.22, 10.31 (2 CH$_3$), 20.05, 27.51, 27.83, 28.34 (4 CH$_2$), 55.66, 55.78, 55.95 (2 OCH$_2$), 58.48, 58.55, 58.67, 58.84 (2 NCH), 64.92, 65.13, 65.39, 65.55 [2 =*C*(CN)], 112.67, 112.72, 114.75, 114.87 (2 CN), 155.04, 155.14, 155.43 (2 =CH), 161.01, 161.68, 162.37, 162.44 (2 C=O). – EI-MS, *m*/*z* (%): 360 (76.8) [M$^+$]. – $C_{18}H_{24}N_4O_4$ (360.4): calcd. C 59.99, H 6.71, N 15.55; found C 59.95, H 6.81, N 15.59.

Diethyl 1,4-Butanediylbis(aminomethylene)bis(cyanocetate) (**13**): According to the general procedure **13** was obtained by reaction of 4.06 g (24 mmol) of ethyl (ethoxymethylene)cyanoacetate with 1.06 g (12 mmol) of 1,4-diaminobutane. Yield: 3.73 g (93%) of white needles, three *E*/*Z* isomers, m.p. 164°C. – IR (Nujol): $\tilde{\nu}$ = 3285 cm^{-1} (NH), 2200 (C≡N), 1680, 1670 (C=O), 1610 (C=C). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.19 (m, 6H, 2 CH$_3$), 1.40–1.60 (m, 4H, 2 CH$_2$), 3.20–3.58 (m, 4H, 2 NCH$_2$), 4.05 (m, 4H, 2 OCH$_2$), 7.68–7.83, 7.96 (m, s, 2H, 2 =CH), 8.68–9.11 (2 br. s, 2H, 2 NH). – ^{13}C NMR (75.5 MHz, [D$_6$]DMSO), occasional overlap of signals: δ = 10.32, 10.41 (2 CH$_3$), 21.83, 22.82, 22.95 (2 CH$_2$), 44.46, 44.59 (2 NCH$_2$), 55.58, 55.91 (2 OCH$_2$), 64.04, 64.23, 64.94 [2 =*C*(CN)], 112.94, 114.37, 115.27 (2 CN), 150.81, 155.61, 156.06 (2 =CH), 161.22, 162.03, 162.71 (2 C=O). – EI-MS, *m*/*z* (%): 334 (32.6) [M$^+$]. – $C_{16}H_{22}N_4O_4$ (334.4): calcd. C 57.47, H 6.63, N 16.76; found C 57.04, H 6.72, N 16.28.

B) *Copper(II) Chelates of Ethyl (Aminomethylene)cyanoacetate Ligands* **11** *and* **14**. – *General Procedure*: A solution of 1.0 mmol of the corresponding ethyl (aminomethylene)cyanoacetate ligands (*E*/*Z* mixtures) **10** or **13** in 40 ml of dry methanol was added to a solution of 0.20 g (1.0 mmol) of copper(II) acetate in 20 ml of dry methanol. After stirring for 3 h the complex was precipitated and filtered, washed with diethyl ether and dried under reduced pressure. In the case of **14** the use of sodium methanolate (2.0 mmol) was necessary to accomplish complexation.

1D-Coordination Polymer **11**: According to the general procedure **11** was obtained by reaction of 0.36 g (1.0 mmol) of **10** with 0.20 g (1.0 mmol) of $Cu(OAc)_2 \cdot H_2O$. Yield: 0.30 g (71%) of violet crystals, m.p. > 260°C. – IR (Nujol): $\tilde{\nu}$ = 2200 cm^{-1} (C≡N), 1630 (C=N), 1520, 1500 (C=C). – EI-MS, *m*/*z* (%): 421 (100) [M$^+$]. – $C_{18}H_{22}CuN_4O_4$ (421.9): calcd. C 51.24, H 5.26, Cu 15.06, N 13.28; found C 50.94, H 5.31, Cu 14.93, N 13.06.

X-Ray Structure Analysis[9] *of* **11**: Dark blue parallelepipeds from methanol/diethyl ether/pentane. Single-crystal dimensions 0.08 ×

0.32 × 0.46 mm, formula $C_{18}H_{22}CuN_4O_4$, M_r 421.94, a = 6.786(3), b = 11.791(8), c = 11.815(9) Å, β = 101.30(7)°, V = 927(1) Å^3, Z = 2, d_{cald} = 1.512 g cm^{-3}. Crystal system monoclinic, space group Pn. Radiation: Mo-K_α, λ = 0.71073 Å, μ = 12.09 cm^{-1}, F(000) = 438, T = 293 K, final R = 0.039 for 1063 observations. The sample was studied with an automatic CAD4 diffractometer by using graphite-monochromatized Mo-K_α radiation. The cell parameters were obtained by fitting a set of 25 high-theta reflections. The data collection ($2\theta_{max}$ = 50°, scan $\omega/2\theta$ = 1, t_{max} = 60 s, range hkl: h = 0 to 8, k = 0 to 14, l = −14 to 14) intensity controls without appreciable decay (0.3%) gave 1867 reflections from which 1063 were independent (R_{int} = 0.023) with $I > 3\sigma(I)$. After Lorentz and polarization corrections the structure was solved by means of direct methods which revealed all the non-hydrogen atoms of the structure. After isotropic (R = 0.095), then anisotropic refinement (R = 0.058), the locations of the hydrogen atoms were determined by a Fourier difference analysis (between 0.41 and 0.16 eÅ^{-3}). The whole structure was refined by full-matrix least-squares techniques (use of F magnitude; x, y, z, β_{ij} for Cu, C, O, and N atoms and x, y, z for H atoms; 243 variables and 1063 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$) with the resulting R = 0.041, R_w = 0.039 and S_w = 1.12 (residual $\Delta\rho \leq 0.27$ eÅ^{-3}).

1D-Coordination Polymer **14**: According to the general procedure **14** was obtained by reaction of 0.33 g (1.0 mmol) of **13** with 0.20 g (1.0 mmol) of $Cu(OAc)_2 \cdot H_2O$ and 2.0 mmol of sodium methanolate. Yield: 0.17 g (42%) of green crystals, m.p. > 260°C. – IR (Nujol): $\tilde{\nu}$ = 2205 cm^{-1} (br., C≡N), 1650, 1620 (C=N), 1560, 1510 (C=C). – EI-MS, m/z (%): 395 (66.5) [M$^+$]. – $C_{16}H_{20}CuN_4O_4$ (395.9): calcd. C 48.54, H 5.09, Cu 16.05, N 14.15; found C 48.04, H 5.01, Cu 16.07, N 14.10.

X-Ray Structure Analysis[9] *of* **14**: Dark green parallelepipeds from methanol/diethyl ether/pentane. Single-crystal dimensions 0.22 × 0.22 × 0.34 mm, formula $C_{16}H_{20}CuN_4O_4$, M_r 395.91, a = 11.015(3), b = 12.023(3), c = 14.524(9) Å, β = 100.18(5)°, V = 1893(2) Å^3, Z = 4, d_{cald} = 1.39 g cm^{-3}. Crystal system monoclinic, space group $P2_1/c$. Radiation: Mo-K_α, λ = 0.71073 Å, μ = 11.80 cm^{-1}, F(000) = 820, T = 293 K, final R = 0.040 for 1765 observations. The sample was studied with an automatic CAD4 diffractometer by using graphite-monochromatized Mo-K_α radiation. The cell parameters were obtained by fitting a set of 25 high-theta reflections. The data collection ($2\theta_{max}$ = 50°, scan $\omega/2\theta$ = 1, t_{max} = 60 s, range hkl: h = 0 to 13, k = 0 to 14, l = −17 to 17) intensity controls without appreciable decay (0.2%) gave 3715 reflections from which 1765 were independent (R_{int} = 0.021) with $I > 3\sigma(I)$. After Lorentz and polarization corrections the structure was solved by means of 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 Fourier differences. After isotopic (R = 0.10), then anisotropic refinement (R = 0.067), the locations of the hydrogen atoms were determined by a Fourier difference analysis (between 0.67 and 0.28 eÅ^{-3}). The whole structure was refined by full-matrix least-squares techniques (use of F magnitude; x, y, z, β_{ij} for Cu, C, O, and N atoms and x, y, z fixed for H atoms; 227 variables and 1765 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$) with the resulting R = 0.044, R_w = 0.040 and S_w = 1.65 (residual $\Delta\rho \leq 0.18$ eÅ^{-3}). Atomic scattering were obtained from International Tables for X-ray crystallography (1974). All the calculations were performed with a Digital Micro VAX 3100 computer by using the MOLEN package (Enraf-Nonius, 1990).

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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, F-35042 Rennes Cedex. Further details concerning the X-ray structure analyses of **11** and **14** may 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.

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