Coordination Polymers, IX[1]

Synthesis and Crystal Structure of a 1D-Sodium Coordination Polymer: $[NaL^4(PMDETA)]_\infty$

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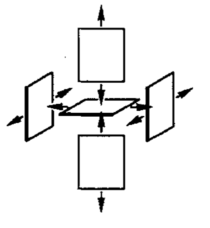
Reaction of sodium hydride with the tridentate tetrazole ligand **10** (HL^4) and pentamethyldiethylenetriamine (PMDETA) in toluene yields by self-assembly in the solid-state the well-ordered 1D-coordination polymer $[NaL^4(PMDETA)]_\infty$ (**11**). The structure of **11** was established by single-crystal X-ray diffraction. The generation of the 1D-polymer **11** is understandable if intermediate formation of coordinatively unsaturated, neutral sodium building blocks $[NaL^4(PMDETA)]$ (**12**) is assumed. Such a self-complementary monomer **12** acts in a monodentate fashion via its CN group, leading to linkage of monomers and to coordinative saturation at the sodium centre of **12**. The sodium ions of the resulting polymeric chains of **11** are coordinated in a distorted octahedral manner. These results indicate that sodium derivatives of CN-containing ligands may be tuned as to their dimensionality, especially so since Na^+ can cope with coordination numbers of 4, 5, or 6; such tuning could be probed initially by provision of further available functionalities within the anionic ligand and/or by provision of Lewis base donors of varying denticity.

The design of self-complementary subunits that self-assemble into well-defined structures in the solid state is of intense interest for the preparation of materials with useful optical or electronic properties[2]. Our current research activities include the development of new strategies suitable for the generation of well-ordered aggregates, nanostructural up to polymeric. As a rule, linkage of the individual building blocks occurs via hydrogen or metal bridges[3].

Recently, we reported on the structures of the 3D-coordination polymer **1** of the general composition $[CuL^1{}_2]_\infty$ (HL^1 = **4**)[4], whereas under exactly the same conditions pyrrolidine **5** (HL^2) forms a 2D-coordination polymer **2** $[CuL^2{}_2]_\infty$[5]. A prerequisite for the generation of 3D/2D-polymers **1** and **2** is the intermediate formation of the coordinatively unsaturated, bidentate copper(II) building blocks **7** and **8**. These coordinate by means of the two cyano groups, leading to linkage of monomers and to coordinative saturation at the copper(II) centres of **7** and **8** with the formation of the corresponding three- and two-dimensional coordination polymers **1** and **2** by self-assembly. In contrast to **7** and **8**, the C_2-symmetric building blocks **9** ($CuL^3{}_2$, HL^3 = **6**) are sterically shielded at one side and thus couple only across one cyano group. This leads to reduced dimensionality and to the formation of the helical 1D-polymer **3** $[CuL^3{}_2]_\infty$[6].



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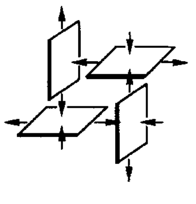

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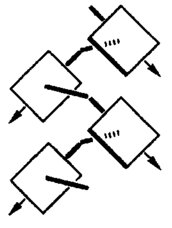

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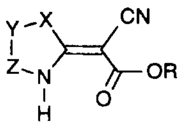

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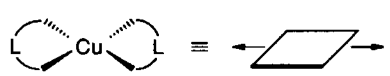

7 - 9

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

We considered that another strategy (aside from steric shielding) by which reduced dimensionality might be achieved would be by using a Group-1 metal. In such a case, regardless of steric considerations, only one cyano group per monomeric unit could be available for coordination to another metal centre. Such a strategy has been successful, and we here report on the synthesis and crystal structure of a 1D-sodium coordination polymer.

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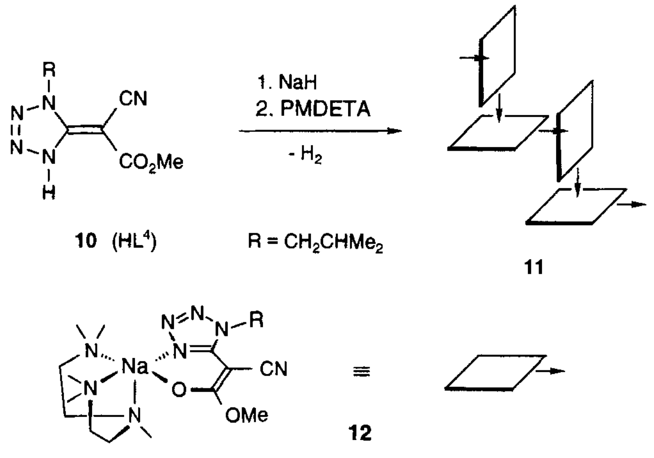
Results and Discussion

The reaction of sodium hydride with the tetrazole **10** (HL^4) in the presence of PMDETA (pentamethyldiethylenetriamine) in toluene leads, after heating to 90°C for 15 min, to evolution of hydrogen and dissolution of the suspended sodium hydride. Cooling to room temperature of the resulting solution gave colourless crystals of **11** suitable for X-ray analysis in good yield (71% for the first crop). These are only sparingly soluble in non-coordinating solvents but very soluble in acetonitrile where depolymerization of **11** presumably takes place. According to the microanalysis, the general composition of product **11** corresponds to $[NaL^4(PMDETA)]_\infty$.



10 (HL^4) R = CH_2CHMe_2 **11**

12

The generation of the one-dimensional coordination polymer **11** is understandable if one assumes the intermediate formation of a coordinatively unsaturated, monomeric sodium building block $[NaL^4(PMDETA)]$ **12**. Prompted by the coordinative unsaturation of the sodium centres, the *self-assembly* of monomers **12** in the solid-state leads to the formation of the neutral 1D-polymer **11**.

The exact structure of **11** was determined by X-ray crystallographic structural analysis[7]. According to this analysis the central sodium ion is coordinated by one tetrazole ligand (L^4, HL^4 = **10**) and the tridentate PMDETA. An intermolecular contact with the CN group of a neighbouring monomer completes the preferred sixfold coordination of the sodium centre. The coordination sphere of the metal ion can be described as a distorted octahedron or as a distorted pentagonal pyramid (Figures 1, 2).

The connecting Na···NC distance amounts to 245.2 pm, and the Na(1)−N(5b)−C(5b) bond angle is 168.3°. An unusual feature is the high Na(1)−N(8) bond length of 267.5 pm; the other Na(1)−N(6,7) contacts of the PMDETA ligand amount to 256−257 pm. The polymeric chains of **11** are arranged parallel to each other in the unit cell (Figure 3).

To the best of our knowledge, **11** is the first sodium tetrazole complex. Only a few nitrile compounds are found among the many structurally characterized organoalkali metal complexes[8], possibly due to the tendency of these compounds to give polymeric products.

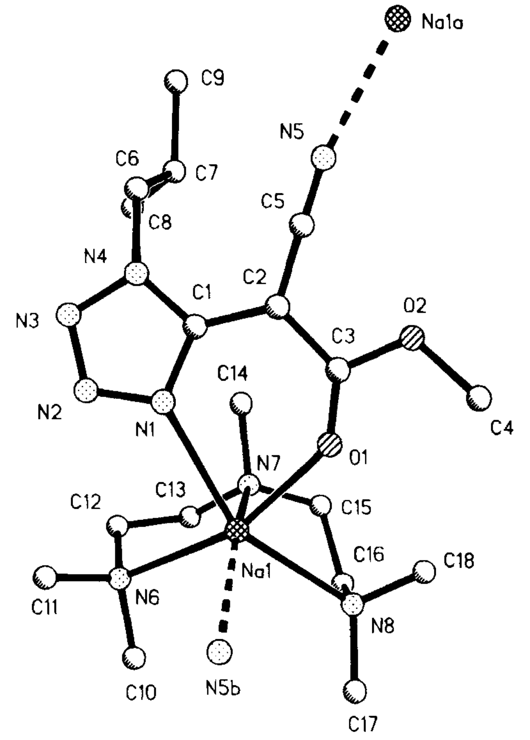


Figure 1. Structure of the monomeric unit of coordination polymer **11** in the crystal (H atoms have been omitted for clarity); selected bond lengths [pm] and angles [°]: Na(1)−O(1) 232.97(1), Na(1)−N(5b) 245.2(2), Na(1)−N(7) 256.0(2), Na(1)−N(1) 256.5(2), Na(1)−N(6) 257.6(2), Na(1)−N(8) 267.5(2); O(1)−Na(1)−N(5b) 106.32(6), O(1)−Na(1)−N(7) 99.55(6), N(5b)−Na(1)−N(7) 147.59(5), O(1)−Na(1)−N(1) 71.14(5), N(5b)−Na(1)−N(1) 115.33(5), N(7)−Na(1)−N(1) 91.15(5), O(1)−Na(1)−N(6) 160.90(5), N(5b)−Na(1)−N(6) 87.91(5), N(7)−Na(1)−N(6) 72.30(6), N(1)−Na(1)−N(6) 91.43(5), O(1)−Na(1)−N(8) 90.53(5), N(5b)−Na(1)−N(8) 90.15(5), N(7)−Na(1)−N(8) 70.17(5), N(1)−Na(1)−N(8) 151.62(5), N(6)−Na(1)−N(8) 102.35(6), C(5b)−N(5b)−Na(1) 168.31(14)

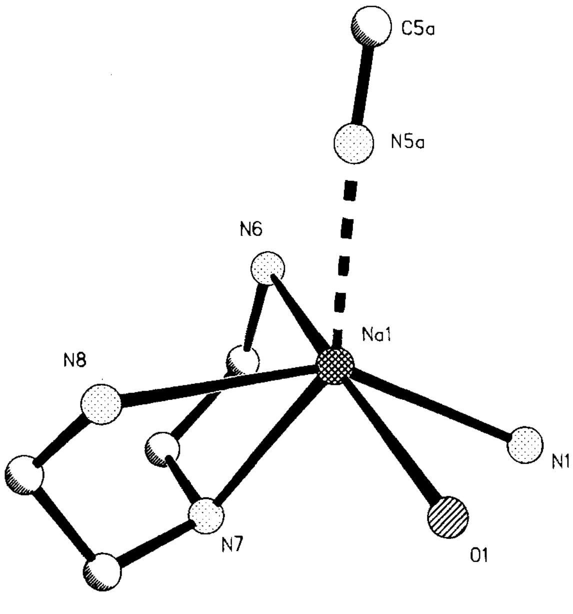


Figure 2. Coordination sphere of the Na centre in the monomeric unit of polymer **11**

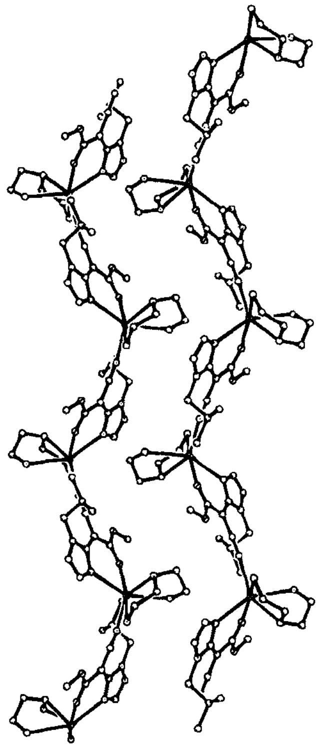


Figure 3. Crystal packing of 1D-coordination polymer **11**

The crystal structure of **11** confirms our initial prediction that polymerization of an alkali metal cyano tetrazole derivative would be only 1D, compared to 2D for the corresponding Cu(II) polymer **2**. It further demonstrates that the *self-assembly* of coordination polymers may be directed very conveniently by a linear cyano group. Sodium derivatives appear to be particularly promising for exploring the factors which allow variable dimensionalities since Na^+ can cope with coordination numbers of 4 through to 6. We will explore such variations by using ligands with further functionalities (e.g., a second CN group) and by using Lewis base donors of lower denticity than PMDETA.

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Experimental

Melting points (uncorrected): Bock Monoskop VS. – IR: Beckman Acculab 1, 3 and 8. – UV: Beckman DU-64. – ^1H NMR: Jeol JNM-GX-400-FT (TMS int.). – ^{13}C NMR: Jeol JNM-GC-400-FT (100.5 MHz, TMS int.). – MS: Varian-MAT CH-48 (direct emission, 70 eV). – Elementary analyses: Heraeus CHN-Mikroautomat.

A) *Methyl (E)-2-Cyano-2-[4,5-dihydro-1-(2-methylpropyl)-1H-tetrazol-5-ylidene]acetate* (**10**) was prepared as described[4a,9]. Yield: 10.1 g (45%) of colourless crystals from CH_2Cl_2/petroleum ether, m.p. 131°C. – IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1} (NH), 2970 (CH), 2200 (CN), 1655 (C=O), 1585 (N=N). – ^1H NMR (400 MHz, $[D_6]$DMSO): δ = 0.89 (d, J = 6.6 Hz, 6H, 2 CH_3), 2.14 (sept, $J \approx$ 7 Hz, 1H, CH), 3.67 (s, 3H, OCH_3), 4.29 (d, J = 7.2 Hz, 2H, CH_2). – ^{13}C NMR (100.5 MHz, $[D_6]$DMSO): δ = 18.90 (2 CH_3), 28.18 (CH), 47.44 (=CC_2), 51.10 (NCH_2), 54.56 (OCH_3), 118.11 (CN), 148.21 (=CN_2), 166.70 (C=O). – EI-MS, *m/z* (%): 223 (30.0) $[M^+]$. – $C_9H_{13}N_5O_2$ (223.2): calcd. C 48.42, H 5.87, N 31.37; found C 48.44, H 5.75, N 30.42.

B) *{2-Cyano-1-methoxy-2-[1-(2-methylpropyl)-1H-tetrazol-5-yl]ethen-1-olato-O,N$^{4'}$}(PMDETA)sodium, 1D-polymer* (**11**): 0.42 ml of PMDETA (2.00 mmol) was added under nitrogen to a suspension of 50 mg (2.08 mmol) of solid NaH and 450 mg (2.00 mmol) of tetrazole **10** in 8 ml of toluene. Stirring for 30 min at room temp. and heating for 15 min at 90°C caused dissolution of the NaH and evolution of hydrogen to give a colourless solution. Cooling at room temp. for 2 h gave crystals of **11** suitable for X-ray analysis, which were washed with toluene and dried in vacuo. Yield: 590 mg (71%) of colourless cubes, m.p. 110–112°C. – IR (Nujol): $\tilde{\nu}$ = 2180 cm^{-1} (CN), 1655 (C=O), 1520 (N=N). – ^1H NMR (400 MHz, CD_3CN): δ = 0.86 [d, J = 6.7 Hz, 6H, 2 $CH(CH_3)_2$], 2.16 [s, 12H, 2 $N(CH_3)_2$], 2.16–2.20 [m_c, 1H, $CH(CH_3)_2$], 2.20 (s, 3H, NCH_3), 2.32–2.35, 2.39–2.43 (2 m_c, 8H, 2 CH_2CH_2), 3.60 (s, 3H, OCH_3), 4.25 (d, J = 7.3 Hz, 2H, N–CH_2CH). – ^{13}C NMR (100.5 MHz, CD_3CN): δ = 19.70 [$CH(CH_3)_2$], 29.43 [$CH(CH_3)_2$], 43.16 (NCH_3), 45.32 (=CC_2), 45.90 [2 $N(CH_3)_2$], 50.69 (OCH_3), 54.81 (N–CH_2CH), 56.04, 57.90 (2 CH_2CH_2), 124.30 (CN), 154.90 (–CN_2), 170.52 (=CO_2). – $C_{18}H_{35}N_8NaO_2$ (418.5): calcd. C 51.66, H 8.43, N 26.77; found C 51.06, H 8.29, N 26.67.

X-Ray Structure Analysis[7] *of* **11**: Colourless cubes from toluene. Single-crystal dimensions 0.6 × 0.6 × 0.6 mm, formula $C_{18}H_{35}N_8NaO_2$, M_r 418.52, a = 1026.8(2), b = 1561.0(3), c = 1492.6(3) pm, β = 97.67(3)°, V = 2371.0(8) · 10^6 pm^3, T = 153 K, Z = 4, d_{calcd} = 1.172 g cm^{-3}. Crystal system monoclinic, space group $P2_1/c$. Diffractometer: Stoe four-circle. Radiation: Mo-K_α, λ = 71.073 pm; programme used: Siemens SHELXTL PLUS; monochromator: graphite. – Range for data collection: [Θ] 4.00 to 22.49°. Index ranges: h = –11 to 11, k = –16 to 9, l = –16 to 16. Reflections collected: 6242; independent reflections: 3076. Absorption coefficient: 0.096 mm^{-1}. R = 0.0420; R_w = 0.0394.

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