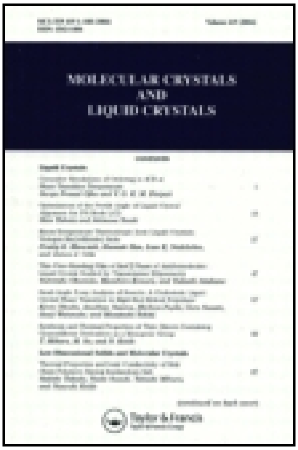

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Molecular Architectures

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MOLECULAR ARCHITECTURES

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Abstract In the last few years we have developed a versatile procedure for the convenient synthesis of numerous tetranuclear chelate complexes on the basis of *spontaneous self-assembly*. The exact structure of the adamantanoid cage compounds was defined by X-ray analysis and their electrochemistry was studied by cyclic voltammetry.
By using the *complexes as metals* and *complexes as ligands* synthetic strategy, we were able to synthesize 3D-, 2D-, and 1D-coordination polymers, respectively, which could be characterized unequivocally by X-ray structure analyses.

INTRODUCTION

The synthesis of supramolecular species from molecular components that possess specific properties is currently attracting great attention as a strategy for developing new materials[1,2].

Transition metal complexes may be appropriate building blocks to synthesize polynuclear metal complexes. New synthetic strategies are needed to obtain supramolecular species which have a well defined number of metal ions and whose specific structures are known by X-ray analysis.

SPHERES AND CAVITIES

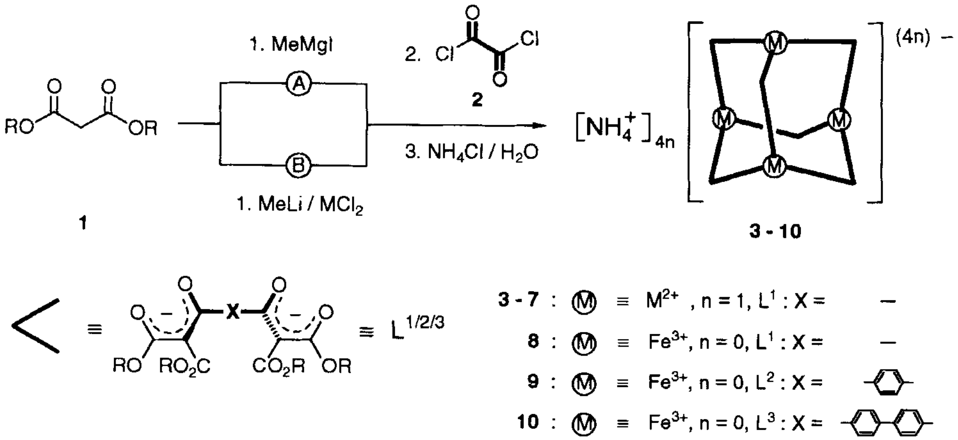
Synthesis and Structures

One of the most interesting new aspects of synthetic chemistry is endohedral chemistry, that is the chemistry in the interior of cages[3]. For that reason, a convenient procedure is required for the construction of cavities of variable diameters.

Reaction of malonic esters **1** with methylmagnesium iodide (route A), followed by addition of oxalyl chloride **2** at - 78°C and subsequent work-up with aqueous ammonium chloride solution, furnished tetraammonium tetramagnesate(4-) chelates **3** $[NH_4]_4[Mg_4L^1_6]$ (Scheme 1)[4]. However, the alkylmetal iodides of Mn, Co, Ni and Zn are less readily available. We have therefore modified our synthetic procedure for **3**, and instead of using methylmagnesium iodide, we now use methyllithium / magnesium chloride (route B). The advantage of this approach is the fact that simple replacement of magnesium chloride by the chlorides of Mn, Co, Ni or Zn, allows the corresponding tetranuclear complexes **4** - **7** to be easily synthesized in good yields (80 to 87%)[5]. The tetranuclear *adamantanoid* chelate complexes **3** - **7** are formed in a one-pot synthesis via *spontaneous self-assembly*[5,6]. The parent, doubly bidentate bridging ligands $[L^1]$ are formally obtained by template coupling of two malonic ester monoanions with oxalyl chloride to give the corresponding tetraalkyl 2,3-dioxobutane-1,1,4,4-tetracarboxylates $[H_2L^1]$, which are spontaneously doubly deprotonated.

Neutral tetranuclear *adamantanoid* chelate complexes with tailor-made cavities should be accessible in substituting the M^{2+}-ion centers by M^{3+}-ion centers, and in going from the parent ligands $[L^1]$ to bidentate chelating ligands enlarged by suitable spacer units $[L^2, L^3]$.

Double deprotonation of tetramethyl 2,3-dioxobutane-1,1,4,4-tetracarboxylate $[H_2L^1$-**a**], tetramethyl 2,2'-(terephthaloyl)dimalonate $[H_2L^2$-**a**], and tetramethyl 2,2'-(4,4'-biphenyldiyldicarbonyl)dimalonate $[H_2L^3$-**a**], in tetrahydrofuran at 20°C with



$L^{1/2/3}$	a	b	c	d
R	Me	Et	${}^tBu$	$CH_2C{\equiv}CH$

	3	4	5	6	7
M^{2+}	Mg^{2+}	Mn^{2+}	Co^{2+}	Ni^{2+}	Zn^{2+}

Scheme 1

sodium hydride and reaction of the corresponding dianions with iron(III) chloride affords red crystals from acetone of **8a** $[Fe_4L^1_6]$[7], **9a** $[Fe_4L^2_6]$[8] and **10a** $[Fe_4L^3_6]$[9], respectively.

The ^1H- and ^{13}C-NMR spectra of **3** - **10** do not establish the structure of these compounds, unambiguously. Therefore, we chose to carry out X-ray structure analyses of the ammonium salts **3b**, **4a**, and **5a**, and neutral tetranuclear chelate complex **9a**. As representative examples, the structures of complexes **5a** and **9a** are shown in Figure 1. Figure 2 shows the stereoview of the crystal packing of **9a**.

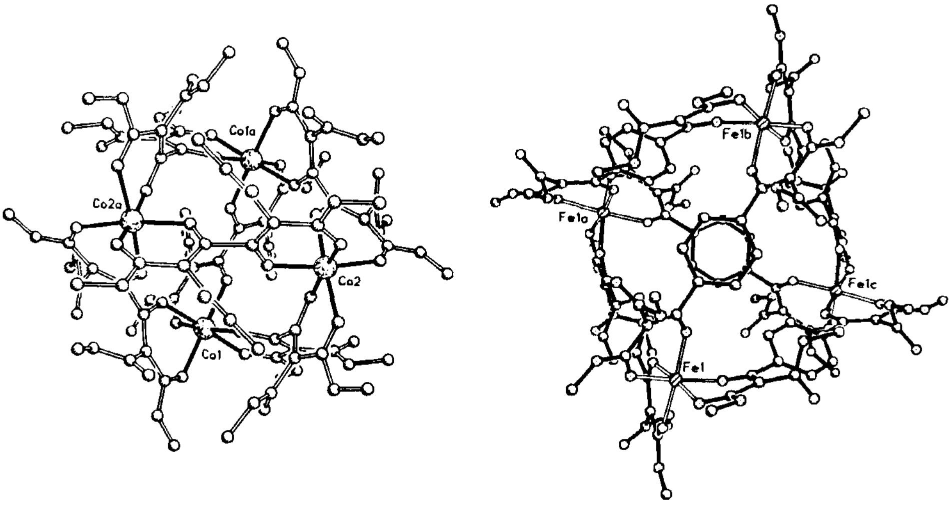


Figure 1. Left: Crystal structure of the tetracobaltate(4-) chelate ion **5a**$^{4-}$ in the crystal (view along the crystallographic C_2 axis; H atoms omitted). Right: Crystal structure of neutral $[Fe_4L^2_6]$ complex **9a** (view along the crystallographic S_4 axis; H atoms omitted).

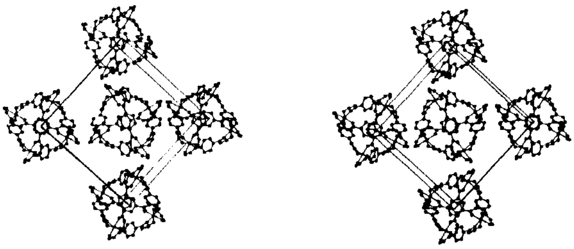


Figure 2. Stereoview of the crystal packing of **9a** (view along the crystallographic S_4 axis; for reasons of clarity the methoxy and methoxycarbonyl groups as well as the solvents of crystallisation have been omitted).

The core of the tetracobaltate(4-) complex ion of **5**$^{4-}$ is a distorted tetrahedron, comprising four cobalt(II) ions. These ions are linked along each of the six edges of the tetrahedron by a doubly bidentate bridge [L^1-**a**], so that each of the four cobalt(II) ions is octahedrally coordinated by six oxygen atoms.

The tetracobaltate(4-) chelate ion **5a**$^{4-}$ has an exact C_2 symmetry in the crystal. If we consider an ideal case, however, the anion **5a**$^{4-}$ can be regarded as almost having T symmetry (characterized by three C_2 and four C_3 axes). The asymmetry of this tetranuclear anion results from the atropisomerism of the ligands [L^1-**a**]. All the six chelate bridges, linking the four Co(II) centers, are twisted in the same sense and have nearly C_2 symmetry.

Octahedral complexes with three identical bidentate ligands of type MA_3B_3 generally exist as two pairs of enantiomers [(Δ)-, (Λ)-*fac* and (Δ)-, (Λ)-*mer*][10]. In the case of the chiral T-symmetric tetrametalate(4-) chelate ions **3b**$^{4-}$, **4a**$^{4-}$, and **5a**$^{4-}$, respectively, all four metal centers are coordinated identically [(Δ,Δ,Δ,Δ)-*fac* and (Λ,Λ,Λ,Λ)-*fac*, respectively]. This contrasts with the achiral S_4-symmetric neutral [$Fe_4L^2_6$]-complex **9a**. In the case of **9a**, the six ligands L^2-**a** are all coordinated in a way that four iron centers are facially coordinated, two of them having identical configuration, each [(Δ,Δ)- / (Λ,Λ)-*fac*].

Only relatively complex molecules can have T symmetry. One of the reasons for the comparative rarity of these higher symmetry, chiral compounds is that the required geometric prerequisites, all of which have to be simultaneously fulfilled, make a *non-directed* formation improbable. All the more surprising, therefore, is the high degree of symmetry that is obtained by the *spontaneous self-assembly* process.

In Figure 3, the topology of the tetranuclear chelate(4-) ions of **3** - **7** and neutral complexes **8** - **10**, respectively, are compared with the spherical tricycle **11**[11]. Whereas the bridgeheads of the tricycle **11** consist of nitrogen atoms, the corresponding bridgeheads of the complexes Mg^{2+}-**3**, Mn^{2+}-**4**, Co^{2+}-**5**, Ni^{2+}-**6**, Zn^{2+}-**7** and Fe^{3+}-**8** - **10** are metal ions.

Figure 3. Left: Topology of the tetranuclear chelate(4-) ions of **3** - **7** and neutral complexes **8** - **10** (schematic). Right: Spherical tricycle **11**.

Electrochemistry

The electrochemical behaviour of the tetranuclear complexes **8a** and **9a** has been studied by cyclovoltammetry and spectroelectrochemistry.

The cyclic voltammogram of **8a** (Figure 4, left) exhibits a quasi reversible four-potential-four-electron-transfer process, indicating that the four chemically identical redox centers are interacting across the ligands [L^1-**a**] [12].

However, in contrast to **8a**, the cyclic voltammogram of **9a** (Figure 4, right) shows a quasi reversible one-potential-four-electron-transfer process, suggesting that the four chemically equivalent Fe^{III} centers do not interact across the phenyl spacers of the ligands [L^2-**a**][8].

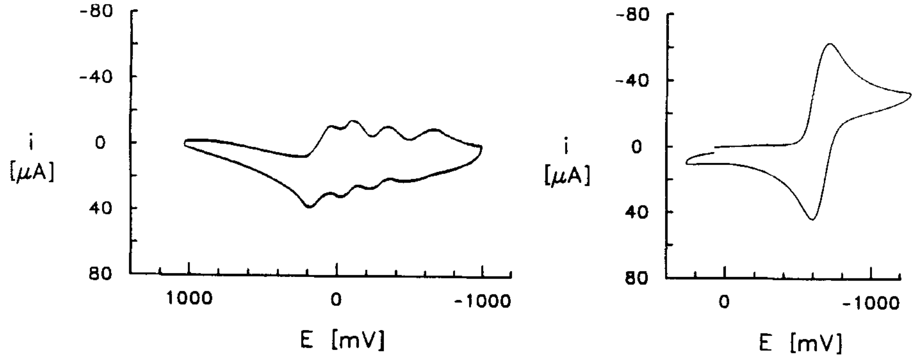


Figure 4. Left: Cyclovoltammogram of **8a**. Right: Cyclovoltammogram of **9a** in a 0.1 M solution of tetraethylammonium tetrafluoroborate in acetonitrile, $c = 10^{-3}$ M, scan speed 250 mVs^{-1}. Potentials vs. ferrocene / ferrocenium (Fc / Fc^+).

Endohedral Complexation

The convenient access of cage compound **9a** prompted us to study conditions for endohedral complexation of small molecules.

Deprotonation of tetramethyl 2,2'-(terephthaloyl)dimalonate [H_2L^2-**a**] in the presence of a small amount of water and subsequent reaction of the dianion [L^2-**a**] with iron(III) chloride affords red crystals from acetone, suitable for X-ray analysis (Figure 5). Therefore, the water molecule of [$H_2O \subset Fe_4L^2_6$] **12a** is centered in the cavity with chloroform in an outside groove[13].

The encapsulation of water obviously occurs during the formation of the cage, since we did not obtain **12a** on simply recrystallizing **9a** from acetone / water.

The endohedral complex **12a** is of particular interest for further studies of complex **8a**, since the FAB-spectra (FAB = Fast Atom Bombardment) of **8a** show peaks at $[Fe_4L^1_6 + Na^+]$, $[Fe_4L^1_6 + K^+]$, and $[Fe_4L^1_6 + NH_4^+]$, respectively, depending on the synthetic procedure employed[7]. The final decision, on whether Na^+, K^+, or NH_4^+, respectively, are incapsulated, awaits a X-ray structure analysis.

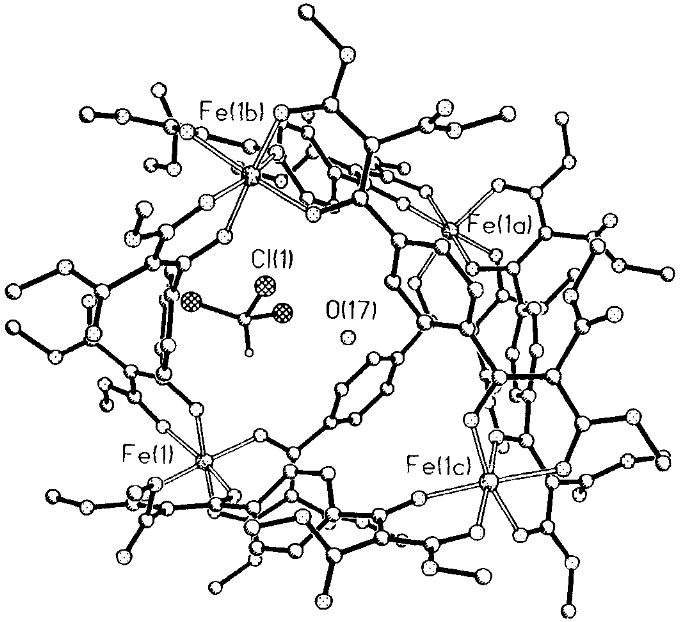
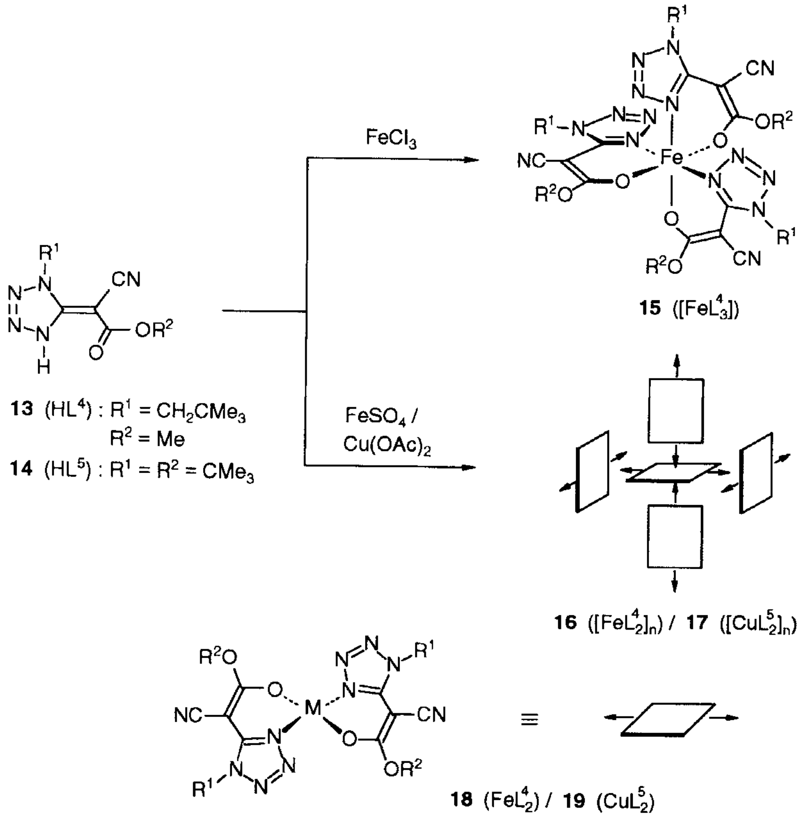


Figure 5. Crystal structure of $[H_2O \subset Fe_4L^2_6]$ **12a** (H atoms omitted, H_2O is centered in the cavity and $CHCl_3$ is located in an outside groove).

COORDINATION POLYMERS

Three-Dimensional Units

Naturally occurring and synthetically accessible siderophores (iron carriers) contain predominantly bidentate pyrocatechinato- or hydroxamato-ligands and are of special interest because of their high affinity towards trivalent metal ions, especially towards iron(III) ions[14]. The (tetrazol-5-yliden)-cyanoacetate **13** (HL^4)[15] appeared to be also suitable as siderophore. Upon reaction of **13** in ether with aqueous iron(III) chloride solution, and, after addition of hexane, **15** separates in the form of deep blue microcrystals. On the basis of the elemental analysis and mass spectroscopic data, **15** is a mononuclear iron(III) complex of the general composition $[FeL^4_3]$ (HL^4 = **13**). In the reaction of **13** with aluminum trichloride, the corresponding aluminum complex $[AlL^4_3]$ is formed. Apparently in each case only the statistically most probable (Δ) / (Λ)-*mer*-isomer of the two theoretically possible (Δ) / (Λ)-configurational isomers is formed[16].



Scheme 2

However, when **13** was treated in diethylether with aqueous iron(II) sulfate solution, a pale green precipitate, which is almost insoluble in noncoordinating solvents, was obtained. According to the microanalysis, the product obtained has the general composition $[FeL^4{}_2]_n$, the FAB-MS data of **16** indicating the presence of a polymer. Whereas **13** functions as bidentate ligand towards iron(III) ions and forms the mononuclear *mer*-complex **15**, the same compound obviously acts as tridentate ligand towards iron(II) ions and affords, by *spontaneous self-assembly*, a polymer. In agreement with a polymeric structure of **16** is the result that **16** is readily soluble in coordinating solvents (Scheme 2)[16].

When a methanolic solution of copper(II) acetate was reacted with (tetrazol-5-yliden)-cyanoacetate **14** (HL^5) [**13** (HL^4) was exchanged by **14** only because of solubility reasons] suitable crystals of polymer **17** ($[CuL^5{}_2]_n$) for X-ray analysis could be obtained from dichloromethane / diethylether[17] (Scheme 2, Figure 6). Therefore, **17** and hence also **16**, are three-dimensional coordination polymers.

The formation of the coordination polymers of type **16** and **17** is understandable if **13** (HL^4), and **14** (HL^5), or their enolates are considered as tridentate chelate ligands and if one assumes intermediary formation of the coordinatively unsaturated building-blocks **18** ($FeL^4{}_2$) and **19** ($CuL^5{}_2$), respectively. The monomers **18** and **19** are bidentate coordinating through the two CN groups, which leads to linking of monomers and to coordinative saturation at the iron(II)- and Cu(II) centers of **18** and **19** with formation of the corresponding three-dimensional coordination polymers **16** ($[FeL^4{}_2]_n$) and **17** ($[CuL^5{}_2]_n$).

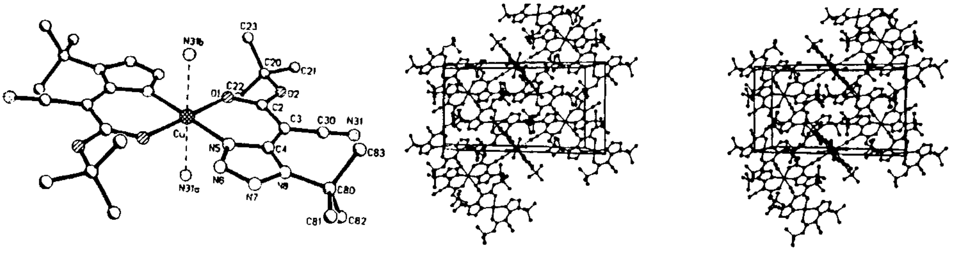


Figure 6. Left: Structure of monomer **19** of coordination polymer **17** in the crystal (H atoms omitted). Right: Stereoview of the crystal packing of **17**.

The Mössbauer spectrum of a powdered sample of complex **16** showed an almost temperature-independent quadrupole doublet with splitting $\Delta E_Q = 3.16$ mms^{-1} in the temperature range 4.2 to 300 K and the isomeric shift $\delta = 1.22$ mms^{-1}, typical for high-spin iron(II) at 4.2 K (Figure 7, left).The δ value confirms the sixfold coordination of the iron by nitrogen and oxygen ligands in the coordination polymer. At 1.6 K without external magnetic field, **16** shows *spontaneous magnetic ordering*, recognizable by the magnetic hyperfine interaction in the Mössbauer spectrum (Figure 7, right), which furnishes further proof of the polymeric structure of **16**. An external field of 0.18 T has no measurable influence on the 1.6 K spectrum of **16**, thus indicating that the magnetic ordering is of an antiferromagnetic nature[16].

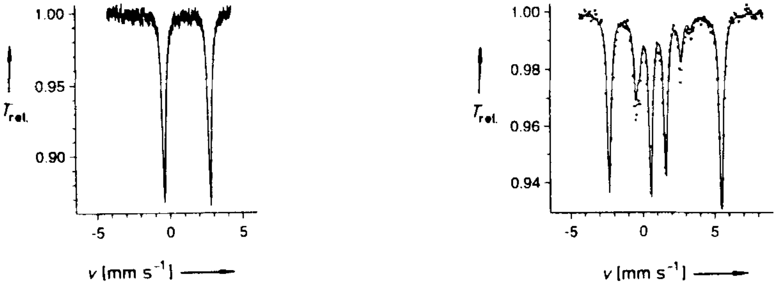
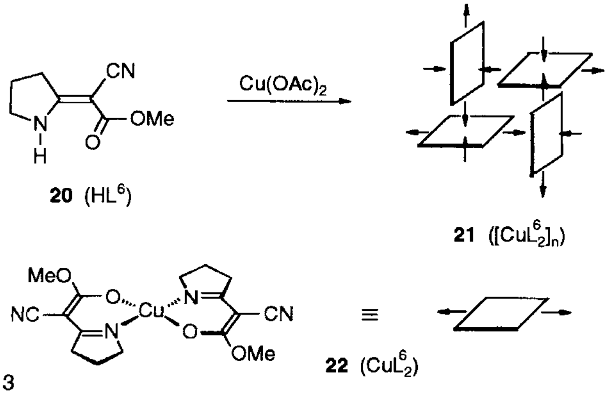


Figure 7. Left: Mössbauer spectrum of a powdered sample of compound **17** ($[CuL^5_2]_n$), recorded at 77 K. Right: Mössbauer spectrum of a powdered sample of compound **17** ($[CuL^5_2]_n$), recorded at 1.6 K.

Sheets

In contrast to (tetrazol-5-yliden)-cyanoacetates **13** (HL^4) and **14** (HL^5) structurally analogous pyrrolidine **20** (HL^6)[18] reacts with copper(II) acetate to give 2D-coordination polymer **21** ($[CuL^6_2]_n$), rather than a 3D-coordination polymer similar to **16** ($[FeL^4_2]_n$), and **17** ($[CuL^5_2]_n$), respectively. The structure of **21** is established by single-crystal X-ray diffraction (Scheme 3, Figure 8)[19].



20 (HL^6)

21 ($[CuL^6_2]_n$)

22 (CuL^6_2)

Scheme 3

The formation of 2D-coordination polymer **21** is understandable if **20** (HL^6) or its enolate is considered as a tridentate chelate ligand and if intermediate formation of the coordinatively unsaturated copper(II) building block **22** (CuL^6_2) is assumed (for further details see the formation of 3D-coordination polymers **16** ($[FeL^4_2]_n$), and **17** ($[CuL^5_2]_n$), discussed earlier).

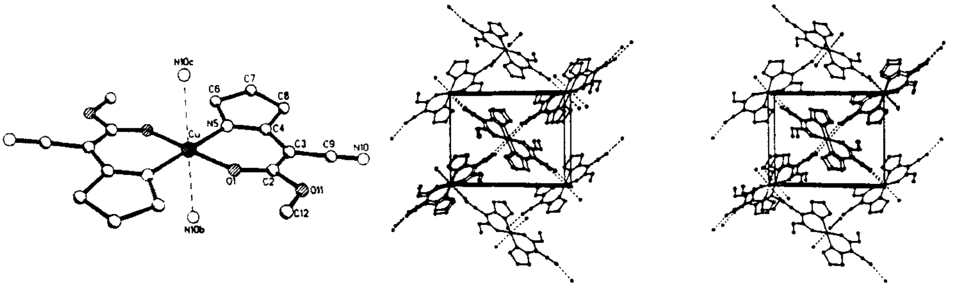


Figure 8. Left: Structure of monomer **22** of polymer **21** in the crystal (H atoms omitted). Right: Stereoview of the crystal packing of **21**.

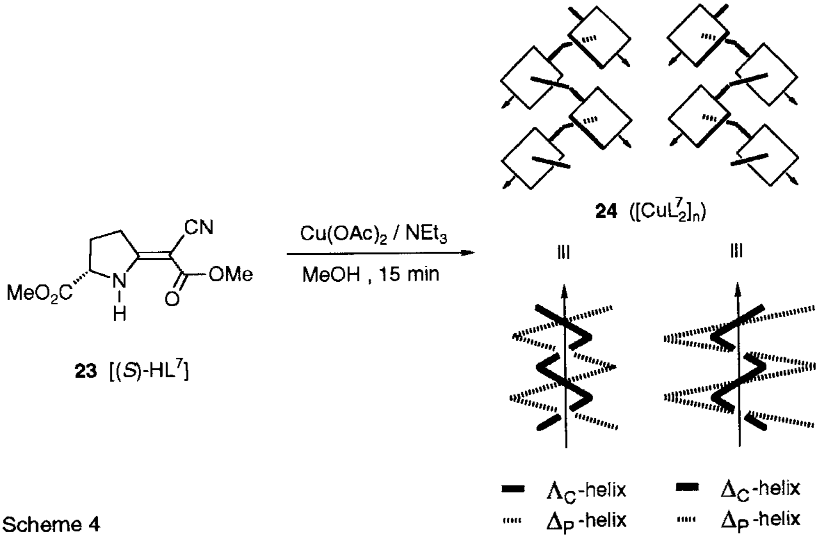
Chains

2D-coordination polymer **21** ($[CuL^6_2]_n$) is insoluble in non coordinating solvents. However, in the presence of excess pyridine, **21** depolymerizes and yields racemic pentacoordinated mono pyridine adduct $CuL^6_2(Py)$[19]. On the basis of pentacoordination at copper(II) we synthesized polymers with reduced dimensionality which have 1D- rather than 2D- or 3D-structures.

Contrary to pyrrolidine **20** (HL^6), ligand **23** [(*S*)-HL^7] reacts with copper(II) acetate to give 1D-coordination polymer **24** ($[CuL^7_2]_n$) (Scheme 4)[20].

The structure of **24** is established by single-crystal X-ray diffraction. Accordingly, there are two, almost identical helix strands (Λ)-Cu(1)-**24** and (Δ)-Cu-(2)-**24** (central helices) in the crystal, consisting of almost identical monomers (Figure 9).

The formation of 1D-coordination polymer **24** is understandable if **23** [(*S*)-HL^7] or its enolate [(*S*)-L^7] is considered as tridentate chelate ligand and if an intermediate formation of a coordinatively unsaturated copper(II) building block, CuL^7_2, analogous to **22** (CuL^6_2), is assumed. The monomers CuL^7_2 are bidentate but at one side sterically hindered. Therefore, contrary to **22**, coordination with only one CN group is possible and leads to linking of CuL^7_2 building blocks and to tetragonal pyramidal coordination at the copper(II) centers of the monomers with formation of 1D-$[CuL^7_2]_n$-**24**.



Scheme 4

Strictly speeking, the helix strands (Λ)-Cu(1)-**24** and (Δ)-Cu-(2)-**24** (central helices) represent a pair of diastereoisomers consisting of C_1-symmetric enolate (S)-L^7 [(S)-HL^7 = **23**] and copper(II) ions. On detailed examination it is realized that the stereogenic centers of the monomers of (Λ)-Cu(1)-**24** as well as of (Δ)-Cu(2)-**24** describe a (Δ)-helix (peripheric helix) [Scheme 4. Bottom: Graphic presentation (schematic) of (Λ)-Cu(1)-**24** (left) and (Δ)-Cu(2)-**24** (right). Central helix (Λ)/(Δ) = ▬, peripheric helix (Δ) = ıııı].

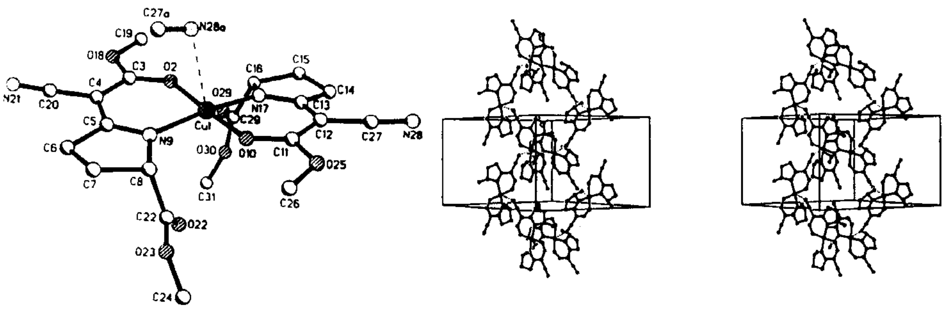


Figure 9. Left: Structure of monomer Cu(1)L$^7_2$ [Cu(2)L$^7_2$ differs only slightly from Cu(1)L$^7_2$ and is not shown] in the crystal (hydrogen atoms omitted). Right: Stereoview of crystal packing of strand (Λ)-Cu(1)-**24** (left) and strand (Δ)-Cu(2)-**24** (right). [For clarity, methoxycarbonyl groups are represented only by their carbonyl carbon atoms. Hydrogen atoms and crystal $(C_2H_5)_2O$ are not shown. Polymer **24** forms a clathrate with $(C_2H_5)_2O$ (stoichiometry: host / guest = 2 / 1)].

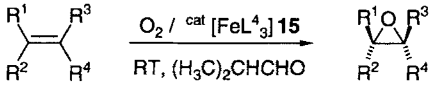
The use of chiral, enantiomerically pure C_2-symmetric monomers could enantiospecifically generate helical 1D-coordination polymers by asymmetric induction. Hitherto, only Cu(I) and Ag(I) chiral, non racemic, helical coordination polymers are known[21].

Catalysis

Metal catalysis of the oxidation of various organic substrates is of synthetic as well as of biological interest[22]. Since the discovery of cytochrome P-450 catalyzed reactions, the unique ability of these enzymes to transfer an O-atom regio- and stereospecifically has been a serious challenge to the organic chemist. Crucial step in simulating P-450 catalyzed reactions is the problematic reductive cleavage of molecular oxygen.

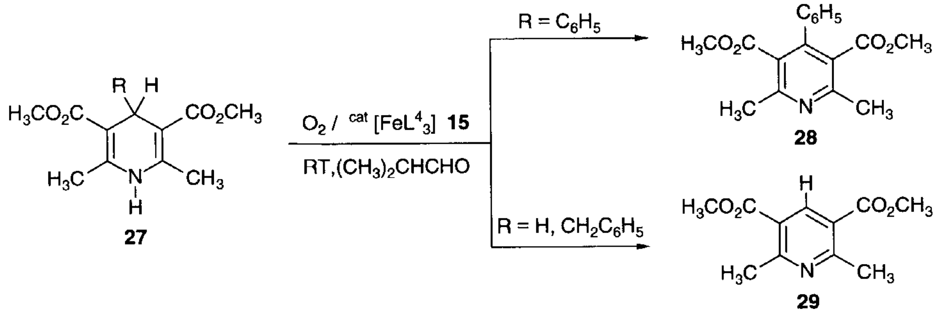
Recent results[23], obtained in the field of oxygenation reactions of hydrocarbons (epoxidation and hydroxylation) catalyzed by synthetic metalloporphyrins or tris(1,3-diketonato)iron(III) complexes associated with various oxidants: single-oxygen donors (iodosylbenzene, N-oxides, hydrogen peroxide, potassium hydrogen persulfate, alkylhydroperoxides) or di-oxygen in the presence of an electron source prompt us to report on our own investigations in this field.

Like cytochrome P-450, synthetic metalloporphyrins or tris(1,3-diketonato)-iron(III) complexes, [$FeL^4{}_3$] **15** is capable in catalyzing the epoxidation of the olefins **25** with combined use of molecular oxygen at atmospheric pressure and an aldehyde at room temperature. The epoxides **26** are generated in good yields (Scheme 5)[24].



Scheme 5

4-Substituted 1,4-dihydropyridines (e. g. *nifedipine*) are important because of their roles as calcium channel blockers. The major products of cytochrome P-450-catalyzed aerobic dehydrogenation of 4-*aryl*-substituted dihydropyridines are the pyridine derivatives, containing the 4-aryl group. In contrast, 4-*alkyl*-substituted dihydropyridines are dealkylated under equivalent conditions[25].



Scheme 6

The biomimetic potential of [$FeL^4{}_3$]-catalyst **15**, in the presence of di-oxygen and isobutyraldehyde has also been studied using dihydropyridines **27** as substrates. The results obtained indicate the formation of products identical to those obtained in the case of *in vivo* metabolism. The dihydropyridines **27** are dehydrogenated or dealkylated to give the pyridines **28** or **29** (Scheme 6)[24].

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