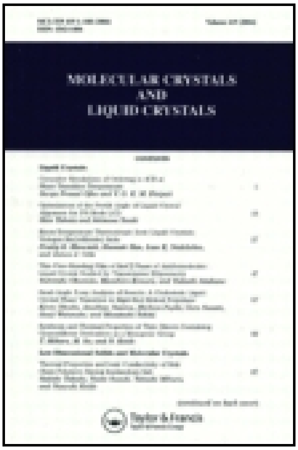

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SYNTHESIS AND PROPERTIES OF CONDUCTING BRIDGED MACROCYCLIC METAL COMPLEXES

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Abstract The synthesis and the properties of polymeric phthalocyaninatometal complexes of the type shown in figure 1 are described. In addition to pyrazine (pyz) and 1,4-diisocyanobenzene (dib) the cyano-group is used as a bridging ligand for the first time such leading to μ-cyanophthalocyaninatocobalt(III) (10). 10 shows a conductivity of 10^{-2} $S \cdot cm^{-1}$ (powder, compressed pellets) at room temperature without iodine-doping.

Recently we presented a new type of phthalocyaninatometal polymers (Figure 1) in which, in contrast to the known type of bridged stacked metallophthalocyanines $[PcMO]_n$ with M = Si^{4+}, Ge^{4+} and $[PcMX]_n$ with M = Al^{3+}, Ga^{3+}, X = F^-) the central metal M now is a transition metal, e.g. Fe^{2+}, Co^{2+} or Co^{3+} and L is an organic bridging ligand, containing π-electrons which are delocalisable. Ligands of this type are e.g. pyrazine (pyz), 4,4'-bipyridine (bpy) or 1,4-diisocyanobenzene (dib)[1] (Figure 1).

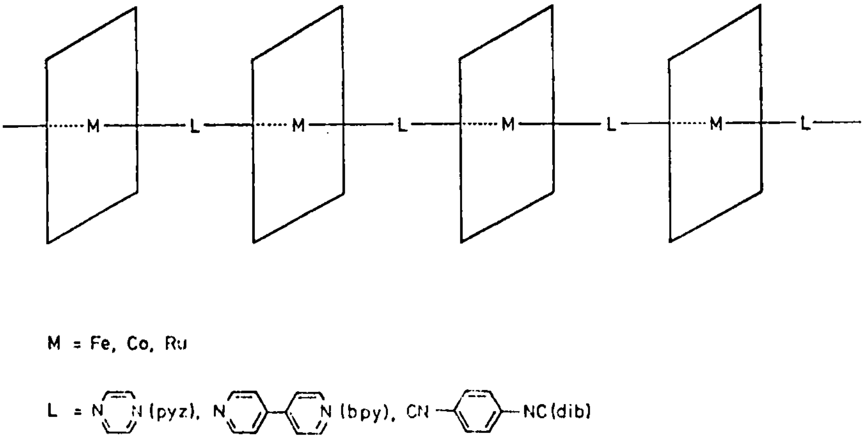

FIGURE 1 A new type of conducting bridged macrocyclic metal complexes.

We became interested in this type of polymer, concerning their conductivities, due to the following reasons:

Bridging ligands containing π-electrons in combination with a transition metal allow a pathway for the electrons along the central axis, which is not the case for the oxygen- and F-bridged polymers $[\mathrm{PcMO}]_n$ and $[\mathrm{PcMF}]_n$. Here the conduction pathway after doping is primarily connected with the macrocyclic ligands,[2] from which a conduction band is formed by π-π-overlap. From the polymers shown in figure 1 therefore we expected conductivities in spite of the fact that the interplanar distances of the phthalocyanine rings within the chain, due to the length of the organic bridging ligands pyz or dib, prevent a π-π-overlap of the parallel Pc-rings.

As we have shown earlier,[1] polymers of the type shown in figure 1 with ▱ = Pc^{2-}, M = Fe^{2+} and Co^{2+}, L =

pyz, bpy and dib, can be prepared. They are stable up to 240°C (for M = Fe and L = pyz) and up to 120°C for M = Co and L = pyz. The polymeric structure for $[PcFepyz]_n$ (1) for example has been proven by TG-DTA-measurements, Mößbauer - spectroscopy and magnetic measurements (the compound is diamagnetic). From IR-studies the degree of polymerisation was estimated to be >20. For $[PcCopyz]_n$ the polymeric structure was deduced from its IR-, NIR- and ESR-spectra,[1] which clearly showed hexacoordination for Co.

$[PcFepyz]_n$ (1) shows a conductivity of $2\cdot10^{-5}$ $S\cdot cm^{-1}$ at room temperature with an activation energy of 0.40 eV (pressed pellets). As shown in table 1 the conductivity of 1, which is 10^7 times higher than the conductivity of $PcFe(pyz)_2$, does not change considerably if the phthalocyanine ring is substituted in the peripherical positions as in 2 and 3.

TABLE 1 Conductivities at RT of differently substituted $[PcFepyz]_n$ polymers

	σ_{RT} $(S\cdot cm^{-1})$
$PcFe(pyz)_n$ 1	$2\cdot10^{-5}$
$(CH_3)_8PcFe(pyz)_n$ 2	$9\cdot10^{-6}$
$(CH_3O)_8PcFe(pyz)_n$ 3	$5\cdot10^{-6}$

Assuming parallel chains in the polymer 1, which was proven for a similar compound $[(DMGH)_2Fepyz]_n$,[3] in 1 exists a possibility for interleaving leading to π-π-overlap of macrocycles of different chains. In 2 and 3 which exhibit the same range of conductivities (without doping) due to the steric requirements of the substituents interleaving is unlikely. Therefore the conductivity of 1 cannot be related to this effect.

The conductivity does not change either if instead of pyz (leading to a distance of 700 pm in between the Pc-rings) dib is used as the bridging ligand (distance Pc-Pc ≅ 1150 pm). $[PcFedib]_n$ (4) shows a conductivity in the same order: $\sigma_{RT} = 2 \cdot 10^{-5}$ $S \cdot cm^{-1}$. These data were interpreted with a conduction pathway along the central axis of polymers 1, 2, 3 and 4.

PcFe reacts with 1,4-diazabicyclo[2.2.2]octane (dabco) in the melt to form the monomer $PcFe(dabco)_2$ (5) or in a solvent, ($CHCl_3$), with formation of the polymer $[PcFedabco]_n$ (6). In contrast to the polymers 2, 3 and 4, 6 contains a bridging ligand without π-electrons. Its conductivity was measured to be 4 powers of ten lower ($\sigma_{RT} = 1 \cdot 10^{-9}$ $S \cdot cm^{-1}$) than that of 1, 2, 3 and 4 but practically the same as the conductivity of the monomer $PcFe(dabco)_2$ (5). ($\sigma_{RT} = 1 \cdot 10^{-10}$ $S \cdot cm^{-1}$).

In addition to Fe and Co, Ru was also used for the first time as the central metal atom.

$[PcRupyz]_n$ (7) shows a room temperature conductivity (powder, pressed pellets, 1 kbar) of $1 \cdot 10^{-5}$ $S \cdot cm^{-1}$, therewith not exceeding the conductivity of $[PcFepyz]_n$ (1).

Table 2 shows the conductivities of the polymers $[PcMpyz]_n$ and the monomers $PcM(pyz)_2$ for different metals:

TABLE 2 Conductivities of $[PcMpyz]_n$ and $PcM(pyz)_2$ (room temperature, compressed pellets, 1 kbar)

$[PcMpyz]_n$	$\sigma_{RT}(S \cdot cm^{-1})$	$PcM(pyz)_2$	$\sigma_{RT}(S \cdot cm^{-1})$
M = Fe	$2 \cdot 10^{-5}$	M = Fe	$2 \cdot 10^{-12}$
M = Ru	$1 \cdot 10^{-5}$	M = Ru	$1 \cdot 10^{-11}$
M = Co	$1 \cdot 10^{-9}$	M = Co	$2 \cdot 10^{-10}$

Polymers of the type shown in figure 1 with pyrazine as the bridging ligand L can also be prepared using instead of phthalocyanine other planar macrocycles e.g. dihydrodibenzo [b,i] -1,4,8,11-tetraaza [14] annulene (taa) as shown for 8. 8 is formed as an insoluble, diamagnetic airstable solid by reacting Fetaa with pyrazine under various conditions.[4]

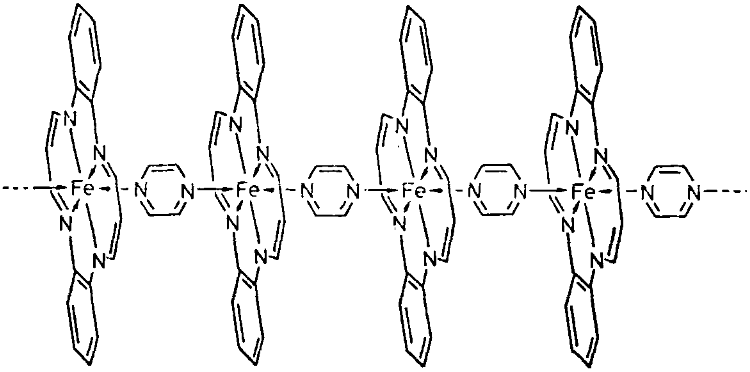

FIGURE 2 $[Fetaapyz]_n$ (8).

8 also shows a room temperature conductivity which is in the same order as the conductivity of the polymers 1, 2, 3 and 7. Beside phthalocyanine comparatively high conductivities of such polymers also can be reached using taa as a macrocycle.

All the polymers described so far with L = pyz and dib as bridging ligands (see figure 1) are coordination polymers. In addition to coordinative bonds the bridging ligand L can be linked to the central transition metal M in figure 1 also by a) two σ-bonds or b) by one σ- and by one coordinative bond. For the type a)-polymer an $C{\equiv}C^{2-}$ could be used as the bridging ligand, for type b) the CN^--group would be a possible candidate.

We have not been successful in preparing a phthalocyaninatoiron(II) polymer with L = $C{\equiv}C^{2-}$. The monomer $Li_2[PcFe(C{\equiv}CtBu)_2] \cdot 7\ THF$ (9) could be synthesized,[5] though 9 is highly sensitive to moisture and oxygen.

In contrast to the type a)-polymer we expected a higher stability for polymers using the CN^--group as a bridging ligand. For this type of polymer cobalt was used as the central metal-atom in combination with Pc as the macrocycle:

The displacement of the axial anion X^- by CN^-, in a coordinatively unsaturated compound of the type PcCoX should be a direct reaction path to the polymeric $[PcCoCN]_n$ (10).

The reaction described for the synthesis of PcCoCl was found to lead to the peripherally chlorinated complex ClPcCo. The published data for the iodine-compound proposed as $Pc^{2-}Co^{3+}I^{1-}$ also agree with the formulation $Pc^{1-}Co^{2+}I^{1-}$ or a nonstoichiometric oxidation of the phthalocyanine moiety. Further compounds of the described type are to our knowledge not reported.

Dichlorophthalocyaninatocobalt(III) is a suitable precursor of the $Pc^{2-}Co^{3+}$-unit which is necessary to build up the described polymer. When $PcCoCl_2$ is heated for three days under reflux in ethanol with an excess of sodium or potassium cyanide, it is converted to $M[PcCo(CN)_2]$(11) (M = Na,K). This compound was characterized by IR, FIR, TG/DTA, NMR and elemental analysis as a monomeric complex salt with terminal cyano groups. When 11 was heated in water in an inert atmosphere for three days under reflux, NaCN was split off and the polymer $[PcCoCN]_n$ (10) formed. The same compound was isolated by the reaction of $PcCoCl_2$ with NaCN in water.

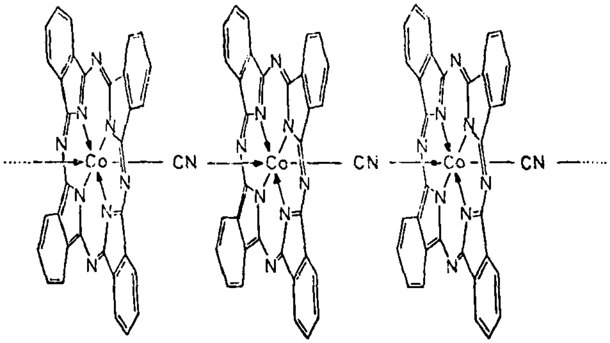

FIGURE 3 $[PcCoCN]_n$ (10).

Evidence for the polymeric structure of 10 was obtained from IR- and FIR-spectra, magnetic measurements and thermogravimetric and microanalytic analysis.

This proposal was confirmed by the synthesis of the monomeric complexes PcCo(L)CN, L = pyridine, methylpyrazine, n-butylamine, piperidine.

The complex $[PcCoCN]_n$ (10) exhibits electrical conductivities around 10^{-2} $S \cdot cm^{-1}$ without iodine-doping, which are comparable with values obtained for doped samples of known μ-oxo and μ-fluoro polymers. When the polymeric structure was decomposed by treatment with a competing ligand to form PcCo(L)CN the conductivity was diminished by 6-10 orders of magnitude.

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REFERENCES

1. a) O. Schneider and M. Hanack, Angew. Chem., 94, 68 (1982).
   b) O. Schneider and M. Hanack, Mol. Cryst. Liq. Cryst., 81, 273 (1982).
   c) J. Metz and M. Hanack, Nouv. J. Chim., 5, 541 (1981).
   d) O. Schneider and M. Hanack, Chem. Ber., in press.
2. C.W. Dirk, E.A. Mintz, K.F. Schoch, jr. and T.J. Marks, J. Macromol. Sci.-Chem., A16, 275 (1981).
3. F. Kubel and J. Strähle, Z. Naturforsch., 36b, 441 (1981).
4. J. Koch and M. Hanack, Chem. Ber., in press.
5. a) R. Taube, H. Drevs and G. Marx, Z. Anorg. Allg. Chem., 436, 5 (1977).
   b) H. Drevs, Dissertation, Greifswald, 1972.
   c) H.-J. Schulze, Diplomarbeit, Tübingen, 1980.