(3) Study mechanisms of polymerization useful for preparing highly conjugated systems with the aim of development of new polymerization processes (photochemical, radiation induced, etc.)

(4) Preparation of novel organic systems with intrinsic conductivity (small band gap).

(5) Synthesize novel dopants (e.g. light or thermally activated, integral part of polymer structure).

POLYMERIC MACROCYCLIC METAL COMPLEXES AS QUASI ONE DIMENSIONAL CONDUCTORS

Scope

Macrocyclic metal complexes can be used as organic conductors (or semiconductors) if they are polymerized in a cofacial arrangement, linked together by bridging ligands. The basic structure is shown in Fig. 1.

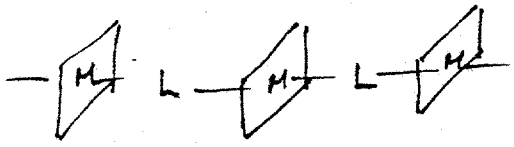

Fig. 1

If M is a transition metal which achieves an octahedral arrangement, e.g. Fe, Ru, Co, Rh, etc., L is a linear organic ligand like pyrazine, 1,4-diisocyanobenzene or CN^- and the macrocycle is ( ); e.g. phthalocyanine, stable polymers (or oligomers) can be synthesized which may exhibit conductivities up to 1 S/cm <u>without</u> additional external doping (M. Hanack et al, since 1980 in various journals).

Polymers of this type have been described first by Kenney and Marks, who used phthalocyanine as the macrocycle, Si, Ge, Sn, Al and Ga as the central metal atom and O and F as bridging ligands. Doping of the corresponding polymers with oxidants, e.g. iodine, led to conductive materials (conductivities up to 1 S/cm).

Justification

The polymeric structure shown in Fig. 1 is highly variable. By changing systematically the three variables, namely the macrocycle M (e.g. from phthalocyanine to tetrabenzoporphyrine, etc.), the central metal atom (e.g. from Fe to Ru) and the bridging ligand L (e.g. from pyrazine to tetrazine), polymers are obtained which, according to MO-calculations, show a band structure (intrinsic conductors). The band-gap can be controlled by the variation of the structure.

Research Proposal

Polymers of the type shown in Fig. 1 should be studied systematically concerning the synthesis and their general properties. By putting substituents in the peripheral positions of the macrocycle, the polymers can be made soluble in most of the organic solvents. The solid state properties, e.g. crystallinity must be studied (if possible). Nothing or only very little is known about the relation between chain length and conductivity.