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SYNTHESIS AND PROPERTIES OF A NEW KIND OF ONE-DIMENSIONAL CONDUCTORS: METAL PYRAZINE AND METAL 4,4'-BIPYRIDINE COMPLEXES

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Polymeric compounds, consisting of square planar metal complexes which are polymerised to linear chains via axial bonded bridging ligands, are new examples for one-dimensional conductors. The synthesis and crystal structure of polymeric bis-(dimethylglyoximato) and bis-(diphenylglyoximato) complexes of Fe(II) and Co(II) with pyrazine and 4,4'-bipyridine as bridging ligands are reported. The Co(II) complexes show only weak bonds in the chain. Stronger bonds, which are essential for the conductivity, are observed for the Fe(II) complexes. Their conductivity is in the range of 10^{-9} $(\Omega \cdot cm)^{-1}$. In addition, polymeric complexes have been synthesized, which consist of only metal atoms and bridging ligands. Examples are the bis-pyrazolate iron(II) and the cationic complex gold(I) 4,4'-bipyridine. Moreover the crystal structure and conductivity of two modifications of monomeric oxo-phthalocyaninato titan(IV) has been investigated.

INTRODUCTION

Recently we published a new concept for one-dimensional conductors[1] consisting of square-planar metal complexes which are polymerized to linear chains by means of axial bonded bridging

ligands.

If the bridging ligand forms an exactly linear chain and possesses a π-system, then continuous conjugation is possible through suitable metal orbitals and even those of the square-planar ligand system. Extended-Hückel calculations[2] show that such complexes can possess a suitable energy-band-structure and therefore conductivity can be expected.

We synthesized the new polymeric bis-(dimethylglyoximato) and (diphenylglyoximato) complexes of iron(II) and cobalt(II) with pyrazine or 4,4'-bipyridine as bridging ligands, which are examples for the new type of one-dimensional conductors. In the case of the bis(dimethylglyoximato) complexes of cobalt(II) the crystal structure has been solved.

In addition the cationic complex gold(I) 4,4'-bipyridine and bis-pyrazolate iron(II) have been prepared. These polymeric complexes consist only of metal atoms and bridging ligands and therefore give information about the influence of the square-planar ligand system to the conductivity.

Only weak conductivity of $5 \cdot 10^{-10} \Omega^{-1}$ cm^{-1} was observed for monomeric oxo-phthalocyaninato-titan(IV). Two modifications of this compound could be obtained and characterized by a crystal structure determination.

POLYMERIC GLYOXIMATO PYRAZINE AND 4,4'-BIPYRIDINE COMPLEXES OF FE(II) AND CO(II)

Synthesis and Properties

By combination of metal(II) sulfate with dimethyl- or diphenylglyoximate in aqueous ammonia as solvent the monomeric diammine complexes are formed. The ammine ligands are easily substituted by adding the calculated amount of pyrazine or 4,4'-bipyridine, whereby the polymeric complexes precipitate.

Measurement of the magnetic properties and Mössbauer spectra prove the iron compounds as being diamagnetic low-spin complexes. The Co complexes are paramagnetic with μ = 1,85 B.M. for cobalt bis(dimethylglyoximato)pyrazine. They

are surprisingly stable against oxidation by O_2 or H_2O_2. The Co complexes do not show conductivity as the bonding in the polymeric chain is very weak. Stronger bonds in the chain occur in the Fe complexes and therefore they are conductors with an approximate value of $10^{-9}\,\Omega^{-1}\,cm^{-1}$. Even higher conductivity of $2\cdot10^{-5}\,\Omega^{-1}\,cm^{-1}$ has been observed recently by SCHNEIDER and HANACK[3] for the similar, polymeric compound phthalocyaninato-pyrazine-iron(II).

Crystal Structure

The crystal structure of bis-(dimethylglyoximato) pyrazine cobalt(II) (Fig. 1) has been published elsewhere[4].

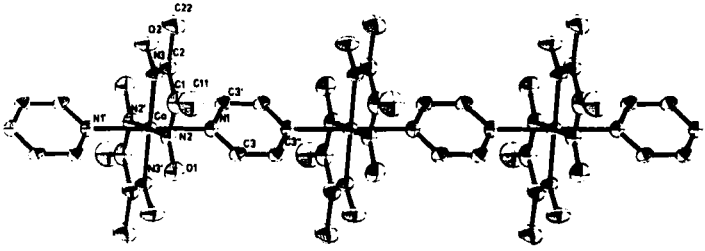

FIGURE 1 Crystal structure of bis-(dimethylglyoximato) pyrazine cobalt(II)

It crystallizes monoclinic in the space group C2/m. The structure is built up by linear chains of alternating Co atoms and pyrazine ligands. Perpendicular to the chain, the Co atoms are coordinated in a square-planar arrangement by two dimethylglyoximato ligands (Co-N = 189 pm), the local symmetry being C_{2h}. The long Co-pyrazine distance of 224 pm is in agreement with the

fact that the compound is a 19 electron complex.

In the face centered lattice the parallel chains of neighbouring polymers are packed in a way such that the plane of the square-planar ligand points to the center of the pyrazine of the next polymer. As a result, short distances of 364 pm between the glyoximato planes occur.

Dimethylglyoximato-4,4'-bipyridine-cobalt(II) crystallizes triclinic in the space group $P\bar{1}$; a = 803,3 ● 0,1 pm, b = 894,2 ± 0,1 pm, c = 895,8 ± 0,2 pm, α = 98,05 ± 0,01°, ß = 91,61 ± 0,01°, γ = 115,47 ± 0,01°, Z = 1.

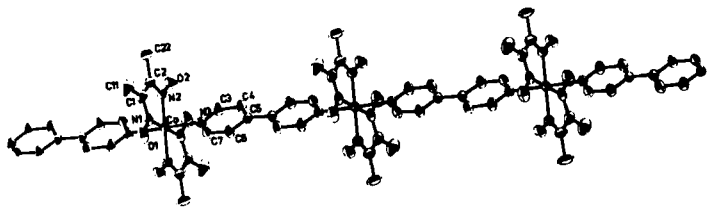

FIGURE 2 Crystal structure of bis-(dimethylglyoximato) 4,4'-bipyridine cobalt(II)

The structure of one chain is shown in Fig. 2. The metal atoms and the central bond of the bipyridine ligand occupy centers of symmetry. The two heterocycles of the bipyridine are therefore co-planar. Again an unusually long distance of 228 pm is found between the Co atom and the bridging ligand. Whereas, the bonds to the nitrogen atoms of the dimethylglyoxime (Co-N = 189 pm) exhibit strong bonds.

THE POLYMERIC, CATIONIC COMPLEX GOLD(I) 4,4'-BIPYRIDINE

The reaction of gold(I)chloride dibenzyl sulfide with 4,4'-bipyridine in ethanol results in the formation of $[Au(bipy)]^+[AuCl_2]^-$. The cation is polymeric and has a linear chain structure (Fig. 3).

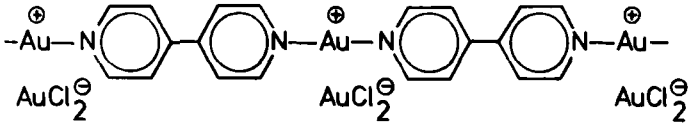

FIGURE 3 Structure of the polycationic complex $[Au(bipy)]^+$

The compound is colorless and not conducting. This indicates that beside strong bonds in the chain, also the square-planar, equatorial ligand system seems to be essential for the conductivity. Similar observation was made for the polymeric bis-pyrazolate iron(II).

POLYMERIC, BIS-PYRAZOLATE IRON(II)

Anhydrous $FeCl_3$ reacts with lithium pyrazolate in toluene to form polymeric bis-pyrazolate iron(II). LiCl and other byproducts are extracted with ethanol. The proposed structure of the compound is shown in Fig. 4. Measurement of the magnetic properties and Mössbauer spectra prove the high-spin character of the complex.The magnetic properties are dependent on temperature and magnetic field strength indicating magnetic coupling between the iron atoms in the chain.

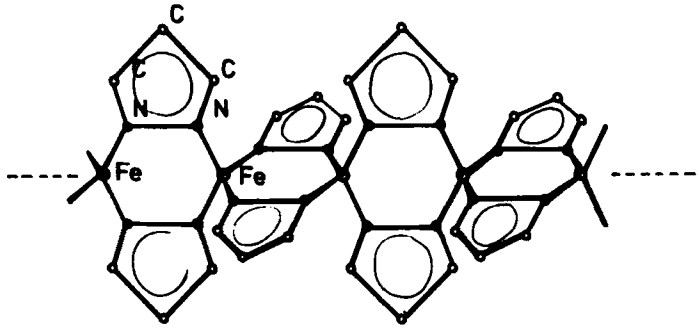

FIGURE 4 Proposed structure of bipyrazolate iron(II)

CONDUCTIVITY AND STRUCTURE OF TWO MODIFICATIONS OF OXO-PHTHALOCYANINATO-TITAN(IV)

Oxo-phthalocyaninato-titan(IV) (PcTiO) shows weak electrical conductivity of $5 \cdot 10^{-10} \Omega^{-1} \cdot cm^{-1}$ at room temperature. Doping with I_2 is accompanied by an increase in conductivity up to $5 \cdot 10^{-3} \Omega^{-1}$ cm^{-1} [5]. PcTiO was found to exist in two modifications built up by monomeric complexes. Phase I (Fig. 5) crystallizes monoclinic in the space group $P2_1/c$. Phase II (Fig. 6) forms a triclinic structure in the space group $P\bar{1}$ which is isotypic with PcVO [6]. In both modifications the Ti atom exhibits square-pyramidal coordination with a short distance Ti-O = 164 pm. Close contacts exist between the phthalocyaninato planes of neighbouring molecules. Detailed results are published elsewhere [5].

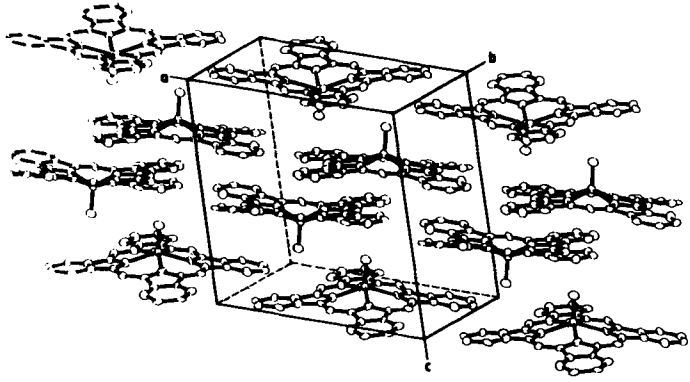

FIGURE 5 Crystal structure of phase I of PcTiO

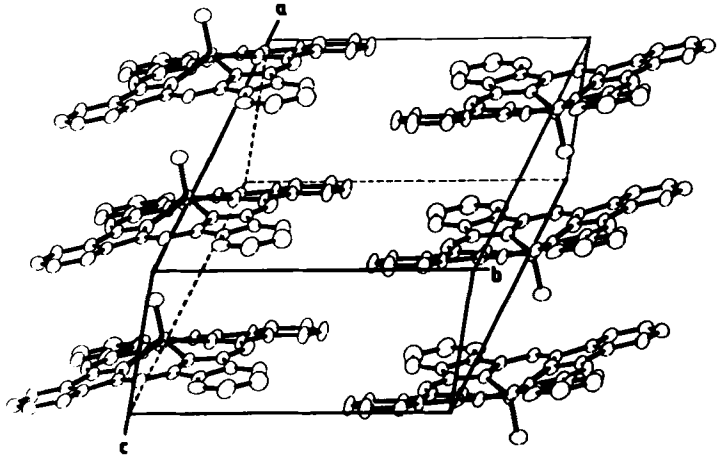

FIGURE 6 Crystal structure of phase II of PcTiO

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