Synthesis and Properties of a New Kind of One-Dimensional Conductors. 1. General Aspects

Michael Hanack
Institut für Organische Chemie

Friedrich Franz Seelig
Institut für Physikalische und Theoretische Chemie

Joachim Strähle
Institut für Anorganische Chemie der Universität Tübingen

A model for a new kind of one-dimensional conductors is presented. The compounds consist of square-planar metal complexes MX_4 which are polymerised via bridging ligands L to linear chains. The bidentate ligand L, e.g. C_2^{2-}, leads to the formation of a linear π-system along the chain, which is essential for the conductivity. The square-planar complex can be, for example, a metal phthalocyanine. MO-calculations show that this kind of polymer gives rise to a suitable energy band structure. An advantage of the new one-dimensional conductors is their flexibility; different combinations of the square-planar ligand system, the bridging ligand, and the central metal atom can be used. First experimental studies show that the preparation of the proposed conductors is possible.

Introduction

Developments in the field of one-dimensional conductors have been rapid in recent years, and several different types are already known. All of them form linear rows of atoms or molecules with small distances which allow the formation of delocalized orbitals in the direction of the row. The so formed energy band has to be incompletely filled near the fermi surface to provide electric conductivity. Some general reviews on this field have already been written [1, 2, 3, 4, 5].

Polymeric complexes like Krogmann's salt $K_2[Pt(CN)_4]Cl_{0,32} \cdot 2,6\ H_2O$ [6], have close similarities to the metals themselves. The conductivity comes from the direct overlap of the d_{z^2}-orbitals of the metal atoms, which thus form linear chains. Each metal atom in addition is surrounded by four ligands in a square planar coordination. Therefore only central atoms with d^8 configuration in a strong ligand field are able to form one-dimensional conductors of this kind. Actually the best known examples are for the metals Pt and Ir, in which the d_{z^2}-orbitals are large enough for a sufficient overlap. As an incompletely filled energy band is essential for the conductivity, the central atoms have to be partially oxidized. A review on this special kind of one-dimensional conductors is given by Krogmann [6].

Analogous to Krogmann's salt is a partially oxidized nickel-phthalocyanine complex [7], in which the phthalocyanine (Pc2-) forces the central atom in a square planar coordination. The highly conductive compound is built up by stacks of PcNi units and chains of polyiodide counterions, so that its formula can be written as $(PcNi)(I_3)_{0,33}$.

This type of one-dimensional conductors is to be distinguished from charge-transfer complexes [8], in which strong electron donors like tetrathiofulvalene are combined with strong electron acceptors such as tetracyanodimethoquinone. The transition of one electron from donor to acceptor leads to the formation of cation and anion radicals, which stack together as alternating columns within the crystal. The direction of conductivity is along the columns, and results from the overlap of π-orbitals on neighbouring radicals. As experience has shown, the charge-transfer complexes are extremely sensitive to impurities; the conductivity as a function of these can vary by orders of magnitude.

Good conductivity along a covalent polymer chain was observed with partially oxidized polymethines [9] and with polymeric sulphurnitride, $(SN)_\infty$ [10]. In the case of polymethines the highest yet known

conductivity for a covalent organic polymer was observed [11].

(SN)$_\infty$ became of great interest, as even superconductivity was achieved at low temperature [12]. It forms endless zig-zag chains of alternating S and N atoms [13]. Strong covalent bonds facilitate the formation of long chains, which are necessary for good conductivity. But changes in conformation might easily occur and diminish the conductivity considerably. The synthesis and properties of (SN)$_\infty$ are reviewed recently [10].

Polymer-Bridged Metal Complexes as a New Kind of One-Dimensional Conductor

In what follows we report on the concept of a new type of one-dimensional conductor which has virtually no freedom to vary its conformation, and in which there is strong bonding within the chains. Moreover they permit a wide-range of possible variants, so that desired properties can be optimised.

This new conductor type consists of square-planar metal complexes which are polymerised to linear chains by means of bridging ligands. The formation of a continuous π-system along the chain, and the conformation stability of these are essential to the property of conduction, and the latter is ensured by the sp-hybridization of the atoms in the bridging ligands.

The principle is shown in a model example. The phthalocyanine (Pc2-) is a square-planar ligand system in whose centre a metal atom can be placed to form the complexes MPc. If M prefers octahedral coordination, then there are two empty coordination sites which can be saturated by bridging ligands L which possess a π-system. Thus infinite one-dimensional chains (PcML)$_\infty$ with conducting properties can be formed. A suitable

bridging ligand is, for instance, the acetylide ion, C_2^{2-}. The resulting polymer is shown in Figure 1.

The proposed new one-dimensional conductor has some similarities with the compounds of the type of the Krogmann's salt and with the partially oxidized polymethines and the polymeric sulphur nitride, as well. But in the proposed new structure there are not so many restrictions limiting the number of possible compounds with good conductivity. Because much more metal atoms prefer an octahedral coordination as there are suitable atoms with a d^8 configuration available. In addition a greater variety of ligands is also possible, since a larger distance between the central atoms allows the use of more bulky ligands. Moreover, as shown, changes in the conformation of the chain are not possible.

If the bridging ligand L (e.g. C_2^{2-}) forms an exactly linear chain and possesses one or even two (crossed) π-systems, then continuous conjugation is possible through suitable metal orbitals and even those of Pc2-. The only criterion for the existence of conductivity in these systems is that the energy bands overlap in the region of the Fermi surface and provide more available levels than there are electrons. The calculations presented in the following paper [14] show that the polymer complexes proposed here can possess a suitable energy-band-structure: In the case of the polymeric phthalocyanin metal acetylide (PcMC$_2$)$_\infty$ the local π-system of Pc2- is perpendicular to both the crossed π-systems of the acetylide ion. So on the one hand only some of the irreducible representations of the π-system from Pc2- are relevant for the one-dimensional infinite conjugation, but on the other hand the orbitals of phthalocyanine especially the lone-pair orbitals of its N atoms, also contribute in part to the conjugation.
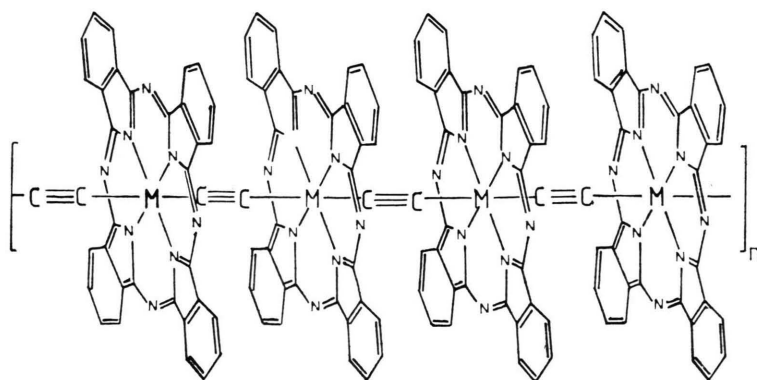

Fig. 1. Drawing of the polymer phthalocyanine-metal-acetylide as a model for a new type of one-dimensional conductor.

The molecular-orbitals of the races a_2, b_1 and b_2 of Pc2-, which are not involved in the conjugation but are highly polarisable, fulfil moreover, one criterion for superconductivity according to Little's theory [15], in which, besides an infinitely conjugated chain which gives rise to normal conductivity, highly polarisable side groups are also necessary.

Similar calculations have been carried out, for comparable polymer complexes with the square-planar ligand-system tetrazaporphin instead of Pc, and with the bridging ligand N^{3-} instead of C_2^{2-}: in these the iterative extended-Hückel-calculation was in part used. These showed that for such complexes conductivity can also be expected.

Wöhrle et al. [16] prepared a polymeric $(PcSiO)_\infty$ in which the planar Si-phthalocyanines are polymerized via bridging O atoms. But the high electronegativity of the O atoms was found to diminish the conductivity. For $[(RNC)_4RhI]^+_\infty$, too, a chain structure is proposed [17]. In this case the bridging I atoms probably have alternating distances to the Rh atoms, which are fairly long.

In the third communication [18] preliminary preparations in the system phthalocyanine-acetylene are described. A series of monomeric trans bis-(1-alkinyl)-4 B-metalphthalocyanines were obtained in the course of preparation of the polymeric $(PcMC_2)_\infty$. These show that it should be possible to prepare the one-dimensional conductor $(PcMC_2)_\infty$.

The proposed new one-dimensional conductor type exemplified by $(PcMC_2)_\infty$ is extraordinarily flexible. Thus bridging ligands with one or two local π-systems other then C_2^{2-} can be used in principle, e.g., the carbodiimido anion, p-aryl-diisocyanide, or homologues of the 1,4-diazines. In the square-planar ligand systems porphine, tetrazaporphine, two bidentate or four monodentate ligands would be appropriate. For the central atom different metals, especially transition metals of suitable charge and size, are possible, in which case the monomeric unit need not be neutral since the excess charge can be compensated by ions outside the chain. This broad flexibility in the new type of one-dimensional conductor allows the properties to be modified as required over a wide range.

[1] H. J. Keller (Editor), Low-Dimensional Cooperative Phenomena. The Possibility of High Temperature Superconductivity, NATO Advanced Study Series **B 7**, Plenum Press, New York 1975.
[2] H. J. Keller (Editor), Chemistry and Physics of One-Dimensional Metals, NATO Advanced Study Series B **25**, Plenum Press, New York 1977.
[3] H. G. Schuster (Editor), One-Dimensional Conductors, Springer-Verlag, Berlin 1975.
[4] J. S. Miller and A. J. Epstein (Editor), Synthesis and Properties of Low-Dimensional Materials, N.Y. Academy of Sciences Conference Proceedings, No. 313, New York Acad. Sci., New York 1978.
[5] E. B. Yagubskii and M. L. Khidekel, Russ. Chem. Rev. **41**, 1011 (1972).
[6] K. Krogmann, Angew. Chem. **81**, 10 (1969); Int. Ed. **8**, 35 (1969).
[7] C. J. Schramm, D. R. Stojakovic, B. M. Hoffmann, and T. J. Marks, Science **200**, 47 (1978).
[8] A. F. Garito and A. J. Heeger, Acc. Chem. Res. **7**, 232 (1974).
[9] C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger E. J. Louis, A. G. MacDiarmid, Y. W. Park, and H. Shirakawa, J. Amer. Chem. Soc. **100**, 1013 (1978).
[10] M. M. Labes, P. Love, and L. F. Nichols, Chem. Rev. **79**, 1 (1979).
[11] H. Shirakava, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, J. Chem. Soc., Chem. Commun. **1977**, 578.
[12] R. L. Greene, G. B. Street, and L. J. Suter, Phys. Rev. Lett. **34**, 577 (1975).
[13] M. Boudeulle, Cryst. Struct. Commun. **4**, 9 (1975).
[14] F. F. Seelig, Z. Naturforsch. **34a**, 986 (1979).
[15] W. A. Little, Phys. Rev. **A 134**, 1416 (1964).
[16] G. Meyer and D. Wöhrle, Die Makromolekulare Chemie **175**, 714 (1974). — M. Hartmann, G. Meyer, and D. Wöhrle, *ibid* **176**, 831 (1975). — G. Meyer, M. Hartmann, and D. Wöhrle, *ibid* **176**, 1919 (1975).
[17] D. Baumann, Thesis, Heidelberg 1974.
[18] M. Hanack, K. Mitulla, G. Pawlowski, and L. R. Subramanian, Angew. Chem. **91**, 343 (1979).