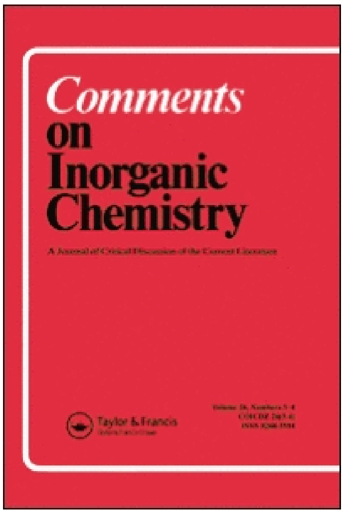

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One-dimensional Inorganic Conductors

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One-dimensional Inorganic Conductors

Extensive theoretical work in the early fifties led to detailed predictions concerning the behavior of one-dimensional metals. More than ten years later the first real systems — linear chain metal complexes — were discovered and many of the predicted pecularities of one-dimensional metals were verified experimentally. Although the initial hope of preparing new, important, and technically useful materials (especially high-temperature superconductors) has not been fulfilled, the results obtained with inorganic compounds triggered the explosive development of organic metals.

Introduction

Physics in one dimension (1d) is exceptional in several respects. First of all, the underlying mathematics is especially simple. The proposed models can very often be treated without approximations on an exact quantitative basis. (A well known example is that undergraduate students are introduced to quantum mechanics through the problem of a particle in a "one-dimensional" box.) Secondly, the physics of 1d systems with collective electron behavior (e.g. metals) is qualitatively very different from the properties of comparable two- or three-dimensional solids. (A simple picture is that a conduction electron in a one-dimensional metal cannot "pass by" or "avoid" another "metallic" electron moving on the same one-dimensional string. Thus strong interactions inevitably occur in 1d collective systems.) The result is the unique physical properties of one-dimensional solids, a group in which the 1d metals pose special questions.

The tractability of the underlying mathematics together with the abnormal behavior expected of 1d metals led to the development of several theoretical models. The results were summarized in detailed predictions of the physical properties of 1d conductors. In particular, the predicted static structural distortion of 1d metals at low temperatures combined with a transition to a nonconducting state[1] ("Peierls" distortion), a giant anomaly in the phonon spectrum[2] ("Kohn" anomaly), and the proposed charge density wave-type

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superconductivity[3] ("Fröhich" superconductivity) aroused the interest of the physics community about twenty five years ago. In addition, the possibility of high-temperature superconductivity ("excitonic" superconductivity) was proposed for specially designed linear conductors,[4] a result which stimulated experimental efforts in the "one-dimensional" field. But until the end of the sixties no real physical systems were available to either prove or disprove the theoretical predictions.

In the sixties, Krogmann described the structures and a few physical properties of some linear chain, mixed-valence platinum complexes,[5] the chemical composition of which had been known for 130 years. They had been recognized as "mixed-valence" materials at the turn of the century.[6] One of the solids, tetracyanoplatinate(II,IV) bromide trihydrate (KCP), was shown to behave like a typical one-dimensional metal in the early seventies[7] and represented the first real system to test all the theoretical predictions. Many groups of transition metal complexes and main group element compounds have since been investigated. (The extensive literature in the field is summarized in a series of conference proceedings[8-14] which also provide a perspective of the historical development.) A short account of success and failure in this field from a more or less personal viewpoint is given here.

Structures, Compounds, and Properties

Candidates for one-dimensional conductors can be readily recognized from their structures. Along the "conduction path" extremely short interatomic or intermolecular contacts should be present, while the interactions perpendicular to the "preferred" direction should be less pronounced. A promising schematic structure is shown in Figure 1, the wide circles representing either atoms or planar molecules. The arrows indicate the direction of preferred interactions (along the stacks) where higher electron densities occur than between the columns. In the more or less "inorganic" structures, three possibilities occur: (1) the conducting compound is a linear polymer made up of atoms or ions of main group elements; (2) the building blocks are planar transition metal complexes. They are stacked on top of each other with their planes adjusted parallel to each other; (3) multichain sytems: linear chain compounds consisting of group (1) and (2) strings. The typical organic metals like TTF–TCNQ or $(TMSF)_2PF_6$ and their derivatives with inorganic counterions are not included in this paper. (See References 8–14)].)]

Main Group Elements

Three highly conducting solids have been characterized so far: $(SN)_x$[15,16], $(CH)_x$[17] (as well as doped derivatives of both) and $Hg_{3-\delta}AsF_6$[18].

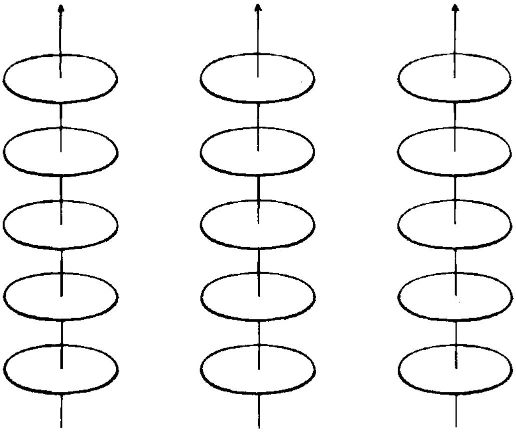

FIGURE 1 Schematic drawing of a "linear" chain structure. The arrows indicate much stronger intrastack interactions compared to interstack exchange.

$(SN)_x$, Polythiazyl As a typical linear polymer, it crystallizes with a pronounced fibrous morphology.[15] In contrast to most other polymeric compounds, it can be obtained as "single crystals" by slowly polymerizing single crystals of the precursor S_2N_2. The arrangement of the two adjacent chain segments is shown in Figure 2(a). The electrical conductivity parallel to the chain direction depends strongly on sample preparation and temperature.

Typical values of the electrical conductivity at room temperature and ambient pressure lie between 1000–4000 Ω^{-1} cm^{-1} (for comparison: copper at room temperature $= 5 \times 10^5$ Ω^{-1} cm^{-1}). The highest value (4000 Ω^{-1} cm^{-1}) is observed after room temperature annealing over a longer period of time. This d.c. conductivity increases by a factor of ~ 250 on lowering the temperature to 4 K. Though composed of the typical nonmetals sulfur and nitrogen, the polymeric $(SN)_x$ behaves as a metal over the entire temperature range studied so far (0.3–300 K). A superconducting transition is observed at about 0.3 K, and the question arose whether $(SN)_x$ would be the first example of an excitonic superconductor. However, a large number of experiments has led to the conclusion that polymeric $(SN)_x$ is an anisotropic three-dimensional semimetal which exhibits bulk Type-II superconductivity caused by the usual BCS (Bardeen, Cooper, Schrieffer) mechanism.[15]

Crystals of $(SN)_x$ can be "doped" (oxidized) by exposure to elemental halogens and the solid-state properties are changed considerably.[16] The d.c. conductivity of $(SN)_x$ crystals exposed to bromine to form $(SNBr_{0.4})_x$ increases by about an order of magnitude to a value of $\sigma_{\|} = 2.4 \times 10^4$ Ω^{-1} cm^{-1} at 300 K and ambient pressure. The superconducting transition appears to be sharper. Detailed structural studies proved that tribromide ions are built into the

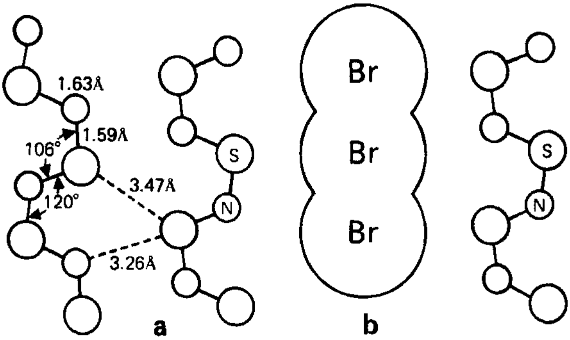

FIGURE 2 (a) Interatomic distances in two parallel chain segments in $(SN)_x$. (b) Possible packing scheme for the Br_3^- ions in the "doped" material.[16]

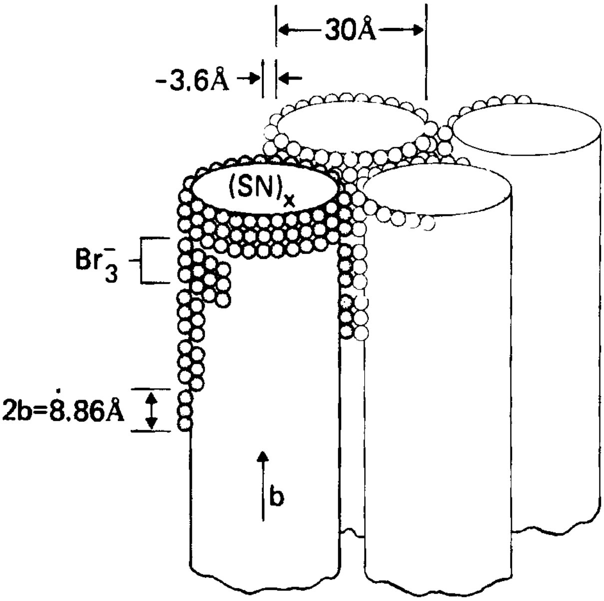

FIGURE 3 Bromine cladding the outside of $(SN)_x$ fibers.[16]

fibrous structure[16] as indicated in Figure 2(b) for the atomic substructure and in Figure 3 for bundles of atomic strings in the solid.

It was not surprising that the unique solid-state properties of a compound made up of two common and cheap nometallic elements initiated extensive research in this field. But one major disadvantage is associated with this type of inorganic conductors: there is no synthetic versatility. $(SN)_x$ and its doped derivatives are "singularities" in this part of the periodic table and no other similar metallic solids have been found since then.

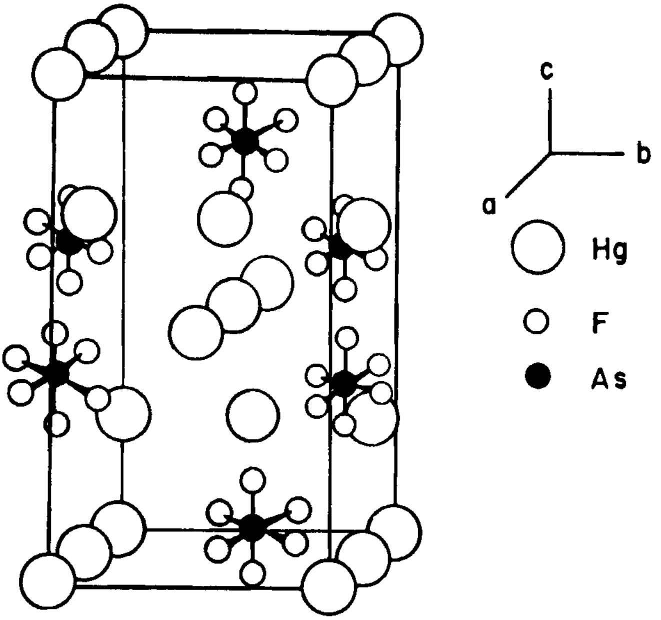

FIGURE 4 Crystal structure of $Hg_{3-\delta}AsF_6$.[18]

$Hg_{3-\delta}AsF_6$ This compound aroused the interest of the physicists mainly because of the strict "one-dimensionality" of its conducting Hg^{n+} spines.[18] Its structure is shown in Figure 4. Linear positively charged mercury chains are situated in nonintersecting channels of the AsF_6^- host lattice along the *a* and *b* axes of the tetragonal structure. The mercury atoms in a chain are incommensurate with the unit cell of the tetragonal lattice, but are well ordered along the chain with a Hg–Hg distance of 2.64 Å. The high conductivity of the compound at room temperature ($10^4\ \Omega^{-1}\ cm^{-1}$) increases with decreasing temperature until transition to a superconducting state is observed at 4.1 K. The analysis of the temperature dependence of the physical properties is complicated by the fact that the Hg content and the overall chemical stoichiometry of the sample changes reversibly with varying temperature. To explain this strange fact in a simple picture, it is convenient to separate the lattice into two parts: a "soft" host lattice composed of the AsF_6^- units, and the stiff (strong bonds between the Hg atoms in the polycations) linear Hg chains. Upon cooling, the "soft" AsF_6^- lattice shrinks more than the "stiff" chains which "stick out" of the crystal's faces with their "ends" covering the surface with mercury.

Many exciting typical 1d effects have been observed during the study of this compound in recent years.[18] Though the material is very interesting scientifically as a typical 1d metal, its sensitivity to moisture and its mercury content make its technical application very improbable and the superconducting transition might well be connected with the elemental mercury at the crystal's surface.

$(CH)_x$, Polyacetylene The situation is totally different for polyacetylene,[17] $(CH)_x$, which, at this time at least, promises possible technical applications. Though it can be viewed as a typical organic compound, it is mentioned in this paper because, like $(SN)_x$, it contains only two nonmetallic main group elements. Thin films of *cis*- and *trans*-polyacetylene can be prepared by solution polymerization of acetylene with a Ziegler–Natta catalyst. The films have a silvery metallic reflectance (like aluminum) and appear blue and red, respectively, in absorption. The polymer has a very open "spaghetti-type" fibrous structure containing many open spaces and the material is not well characterized structurally (chain length, C–C-branching, sp^3 carbons, etc.). Though films of both isomers are poor conductors when pure, doping (oxidizing) with many oxidizing agents (acceptors like AsF_5, I_2) increases the conductivity appreciably and leads to highly conducting metal-like solids even at low temperatures. Because of the ease of preparation and the availability of the starting materials their discovery was considered recently as one of the most important achievements in modern solid-state physics.

Solid Planar Transition Metal Complexes

Compounds These solids are composed of columns which contain planar (mainly four-coordinate) complex molecules (the wide circles in Figure 1) stacked on top of each other and can be regarded as "molecular" solids (they can be dissolved and recrystallized as "molecular" solids), with strong 1d interactions along the central metal spine. With the exception of the partially oxidized phthalocyaninato metal compounds (which mainly interact through their organic ligand systems and not through their metal ions,[19] and should therefore be considered mainly as "organic metals"), highly conducting materials composed of transition metal complex have only been obtained with the very expensive and rare central metals platinum and iridium. This considerably reduces the chances for their widespread technical application. Two principal structures occur: "directly" and "indirectly" interacting (ligand-bridged) types (Figure 5a, b). Ligand bridging (indirect interaction) results if the molecular planes are inclined by an angle appreciably different from 90° to the stacking direction. (This corresponds to a "slipping" of molecular planes in a direction perpendicular to the chain axis). In this case, donor atoms of neighboring molecules occupy the "axial" position above and below a central

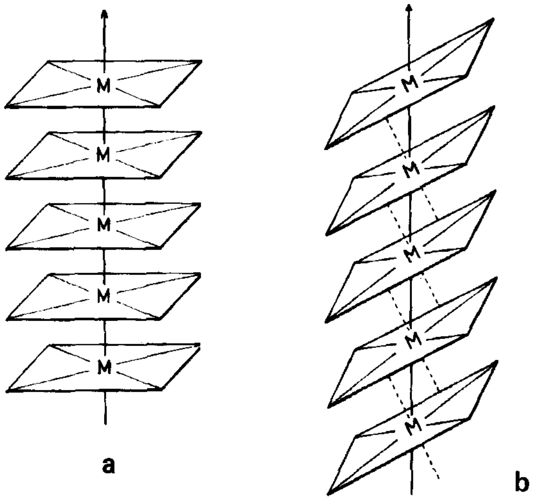

FIGURE 5 (a) Directly interacting metal ions in chains with molecular planes perpendicular to stacking direction. (b) Ligand-bridged interactions in "slipped" structures.

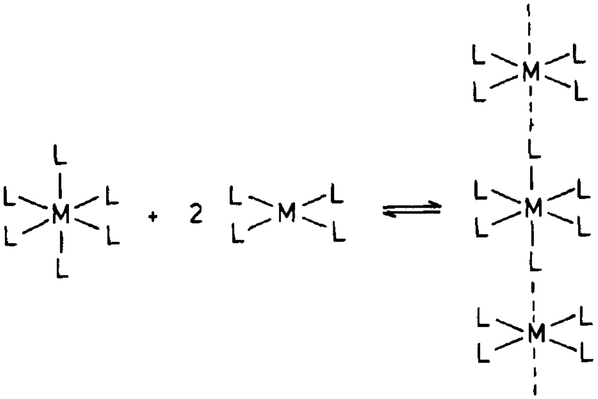

FIGURE 6 Addition reaction of planar four-coordinate molecules with octahedral complexes results in ligand-bridged linear structures.

metal atom (Figure 5b) and a conduction path has to involve the intervening ligand atoms. Another ligand-bridged linear chain is obtained by mixing planar four-coordinate with octahedral molecules, the metal centers having two different oxidation states (Figure 6). [Well-known examples include Wolffram's salt analogs with platinum(II) and platinum(IV) as central ions.[9,10]] Again, any collective properties have to include interactions through the bridging ligands.

So far, highly conducting materials have been found only among the

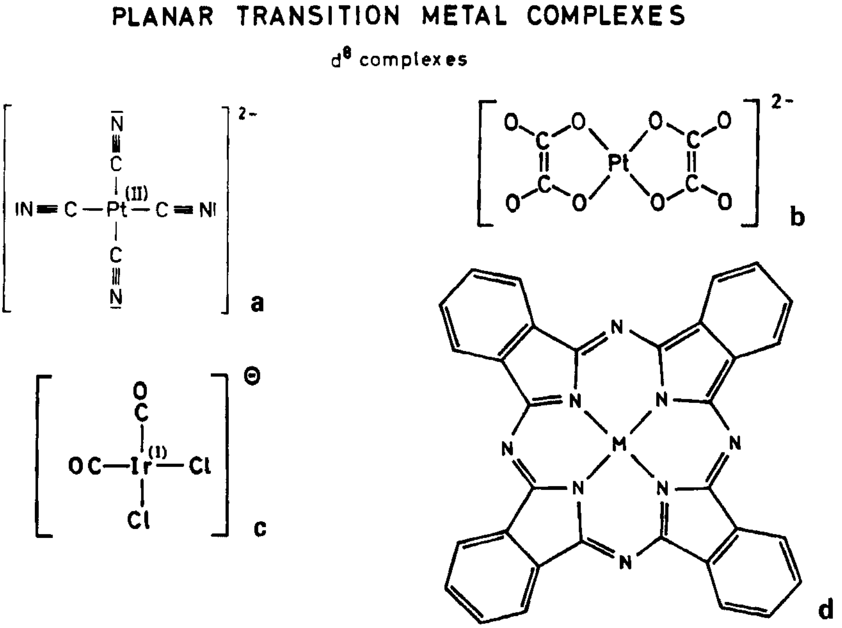

FIGURE 7 Schematic structure of planar (a) tetracyanoplatinate(II), (b) bisoxalatoplatinate(II), (c) dicarbonyldihaloiridate(I), and (d) phthalocyaninatometal(II) complex.

"directly" interacting metal complexes with strong M–M overlap (M–M distances below 2.9 Å). In addition, most of the conducting solids are of the "mixed-valence" type and there has been a long controversy whether 1d metals with integer oxidation states of the central metal atoms exist at all. At least one example, the semimetal $Ir(CO)_3Cl$, is known,[20] and there seems to be no reason why other semimetals should not exist.

The main chemical problem is the absence of a rational synthetic approach to the preparation of 1d structures, especially directly interacting 1d metals, starting with individual planar molecules. Though many experiments have been carried out with the aim of finding a rational way to new materials, the known one-dimensional metals arose accidentally. These are mainly:

(1) Tetracyanoplatinates(II,IV)[21]
(2) Bis(oxalato)platinates(II,IV)[22]
(3) Dicarbonyldihaloiridates(I,III)[23]
(4) Phthalocyaninatometal(II) species and their partially oxidized derivatives[19]

The principal planar building blocks, which are stacked on top of each other in these "linear" solids, are shown in Figure 7 (with a d^8 central metal ion). The composition of the compounds is very complicated in most cases because the

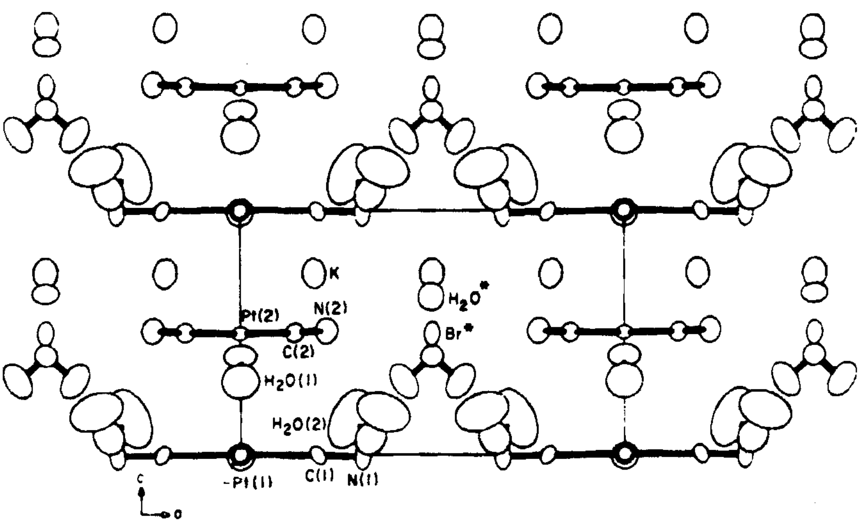

FIGURE 8 Projection of the half-cell of $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$ (KCP) along the *b* axis (perpendicular to the Pt chains). The disordered Br^- and H_2O sites are labeled Br* and H_2O*. (Reference 21).

highly conducting solids contain the transition metal ions in nonintegral oxidation states (mixed-valence solids).

Without any doubt one of the mixed-valence tetracyanoplatinates(II,IV) — $K_2[Pt(CN)_4]Br_{0.3} \cdot 3.0H_2O$ (KCP) (Figure 8) — is the most famous inorganic 1d metal.[7,21] It was the subject of hundreds of investigations during the last decade, and its crystal habit and structure appeared on the front pages of several quite popular scientific journals. The reader is referred to the extensive literature[7-13] for detailed information concerning this important compound.

Structural Studies The elucidation of the X-ray structures of these materials is not a trivial task. Disorder phenomena pose a difficult problem. Two sources of disorder have to be considered.

Nonstoichiometry As mentioned above, most of the highly conducting species are of a "mixed-valence" type. This means that they contain certain metal ions in different formal oxidation states but in very similar or identical site geometries. In summing over the metal ions, fractional oxidation states result and, therefore, the stoichiometric formulae contain non-integral numbers of counterions which occur outside the stacks. In some cases, quite a number of different lattice sites are occupied statistically (in some cases even by different molecules[21]) (Figure 8). Higher lattice symmetries are simulated in the X-ray pictures and the interpretation of the data is complicated by these

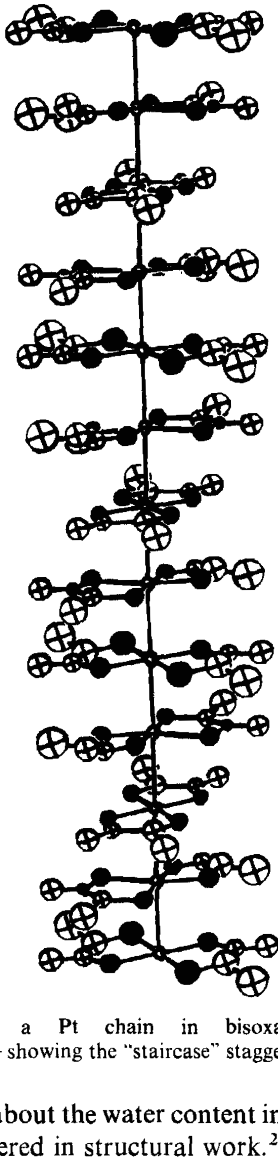

FIGURE 9 Section of a Pt chain in bisoxalatoplatinate(II,IV) hydrate — $K_{1.6}[Pt(C_2O_4)_2] \cdot 1.2H_2O$ — showing the "staircase" staggering network of oxalate ligands.[22b]

facts. The controversy about the water content in KCP is a typical example of the difficulties encountered in structural work.[21]

Disorder along and between Chains There can be disorder along the chains if the symmetry of the planar complex molecule is low (like D_{2h}) and the molecules are stacked along the chains with "torsion angles" which differ from exactly 90° or 180° ("eclipsed" or "staggered" arrangements of the molecules along the stack). The disorder along one chain then adds a modulation which may or may not be commensurate with the crystallographic repeat unit along the stacks. An impressive example of this kind of problem is the structure of the bis(oxalato) platinates(II,IV)[22] (Figure 9). A different kind of structural disorder along the directions perpendicular to the stacks originates in the weakness of the three-dimensional correlations between the chains compared to the strong intrachain interactions. The latter might lead to completely "ordered" one-dimensional chains but with the structure disordered in the other two directions. Parallel neighboring chains might be "slipped" by a certain amount with respect to each other. This "slipping" of chains can occur "statistically" or "regularly" in a direction perpendicular to the chains. The latter gives rise to a three-dimensional "superstructure". Information about these varying three-dimensional correlations is contained in diffusive streaks between or on the Bragg layers of the X-ray pictures. Temperature dependent analysis of the X-ray "diffusions", though very complicated, has helped considerably to understand the properties of these compounds.[24]

Linear-Chain Solids Composed of Two Different Chains

Some of the linear-chain solids can be oxidized to highly conducting "mixed-valence" compounds using iodine or transition metal compounds as oxidants. In some cases, linear polyiodides are built into the channels between the metal chains to counterbalance the additional positive charges on the metal complexes. Detailed structural and physical investigations have shown that linear chains of tri-, tetra-, and pentaiodides occur (Figure 10 shows an example with triiodides[25]). Either linear strings (the polyiodide or the metal chains) could be responsible for the unusual properties of these materials. On the basis of detailed physical investigations, it is believed that the cooperative phenomena are caused solely by interactions along the metal stacks. The compounds have been regarded as model systems for the blue starch-iodide complex.

Other multichain structures can be obtained by using $CuBr_2$ as oxidant.[26]

Electrical Conductivities

Without discussing the numerous results of d.c. and a.c. conductivity measurements, one can state in summary that the bulk conductivity of all linear-chain transition metal complexes is quite low compared to the doped $(CH)_x$ and $(SN)_x$ solids. Exceptions are again the phthalocyaninato metal complexes which should be compared with typical organic metals because of their ligand-ligand interations. An explanation for the low bulk conductivities

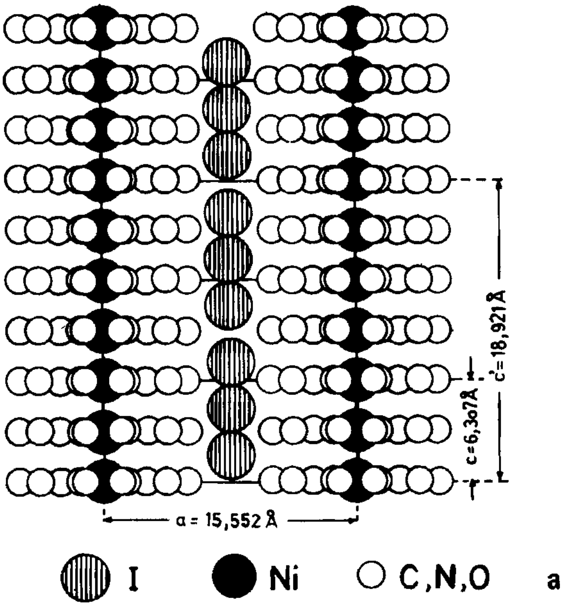

FIGURE 10 (a)) Projection of two metal complex chains and a triiodide chain in bis(1,2-benzoquinonedioximato)nickel(II,IV) iodide onto the *ac* plane. (b) Projection of the structure onto the *ab* plane.

was given earlier in terms of the small diameter of the actual conducting part of the columns compared to the huge and practically insulating ligand contributions of the structures.[27] Taking into account the fact that only a minor part of the columnar structure is actually conducting (the interacting metal ions) quite high electron densities and mobilities occur along the central conducting spine.

A prerequisite for high conductivities are short metal–metal contacts in directly interacting systems. As a general rule M–M distances below 2.9 Å lead to highly conducting materials, independent of the degree of partial oxidation.

Conclusion

Many new "inorganic" solids, which behave like very anisotropic (one-dimensional) metals and which contain essentially linear arrays of atoms or molecules, have been found and investigated recently.

Some of them, $(CH)_x$, $(SN)_x$, and their doped derivatives, contain typical nonmetals as constituents only. These highly conducting polymers might replace conventional metals in some technical applications. Since details of

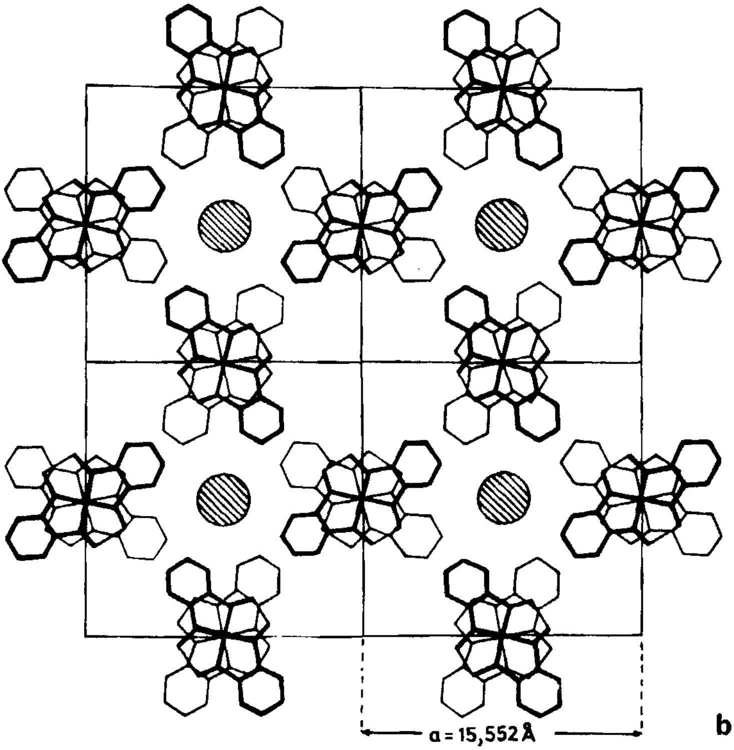

FIGURE 10(b)

their structures and conduction mechanisms are still controversial, a vivid discussion is taking place in this area.

In some other one-dimensional conductors, the conducting path is made up of interacting metal ions which are also good conductors as elements (e.g. platinum and its complexes). The latter compounds have been of interest because the three-dimensional interactions are very weak. These solids are almost perfectly suited for the study of special one-dimensional effects in collective electron systems. Because of their very anisotropic properties they have been, and possibly will continue to be, of basic scientific interest. Beyond this it is doubtful whether they will find any technical applications. The chemistry and physics of these materials are quite well understood and this section of the field appears to be more or less "completed" at this time.

The situation is totally different for the typical organic conductors like TTF-TCNQ and especially for its superconducting derivatives (TMTSF-BF_4[28] and TMTSF-ClO_4[29]) which are just at the beginning of a very promising development. The interest in these solids is not restricted to their anisotropic but extends also to their "bulk" properties.

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References

1. R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, Oxford, 1955).
2. A. M. Afanasev and Yu. Kagan, Sov. Phys. JETP **16**, 1030 (1963).
3. H. Fröhich, Proc. Roy. Soc. A **223**, 296 (1954).
4. W. A. Little, Phys. Rev. A **134**, 1416 (1964).
5. K. Krogmann, Angew. Chem. **81**, 10 (1969); *ibid*, Angew. Chem. Int. Ed. **8**, 35 (1969).
6. A. Werner, Z. Anorg. Chem. **12**, 46 (1896).
7. H. R. Zeller, Adv. Solid. State Phys. **13**, 31 (1973).
8. *Extended Interactions between Metal Ions in Metal Complexes*, ed. by L. V. Interrante (A.C.S. Symposium Series **5**, American Chemical Society, Washington D.C., 1974).
9. *Low-dimensional Cooperative Phenomena*, ed. by H. J. Keller, (NATO–ASI Series **B7**, Plenum Press, New York, 1975).
10. J. S. Miller and A. J. Epstein, Prog. Inorg. Chem. **20**, 1 (1976).
11. *Chemistry and Physics of One-Dimensional Metals*, ed. by H. J. Keller (NATO–ASI Series **B25**, Plenum Press, New York 1977).
12. *Synthesis and Properties of Low-dimensional Materials*, ed. by J. S. Miller and A. J. Epstein (*Ann. N. Y. Acid. Sci.* **313**, 1978).
13 *Molecular Metals*, ed. by W. A. Hatfield, (NATO Conference Series VI, Materials Science **1**, Plenum Press, New York, 1979).
14. *The Physics and Chemistry of Low-Dimensional Solids*, ed. by L. Alcàcer (NATO–ASI Series **C56**, D. Reidel Publishing Company, Dordrecht, Holland, 1980).
15. R. L. Greene and G. B. Street, in Reference 11, pp. 167–196.
16. G. B. Street and W. D. Gill, in Reference 13, pp. 301–326.
17. A. J. Heeger and A. G. McDiarmid, in Reference 14, pp. 353–402.
18. (a) A. J. Heeger and A. G. McDiarmid, in Reference 13, pp. 419–454; (b) V. J. Emery and G. Shirane, in Reference 13, pp. 455–469.
19. B. M. Hoffman, T. E. Phillips, C. J. Schramm and S. K. Wright, in Reference, 13, pp. 393–398.
20. A. H. Reis, Jr., V. S. Hagley and S. W. Peterson, J. Am. Chem. Soc. **99**, 4184 (1977).
21. (a) R. K. Brown and J. M. Williams, Inorg. Chem. **18**, 1922 (1979); (b) J. M. Williams and A. J. Schultz, in Reference 13, pp. 337–368, and references cited therein.
22. (a) A. Kobayashi, Y. Sasaki and H. Kobayashi, Bull. Chem. Soc. Jap. **52**, 3682 (1979), and references cited therein; (b) A. H. Reis, Jr., S. W. Peterson and S. C. Lind, J. Am. Chem. Soc. **98**, 7839 (1976).
23. A. Rosencwaig, A. P. Ginsberg and J. W. Koepke, Inorg. Chem. **15**, 2540 (1976), and literature cited therein.
24. B. Renker and R. Comès, in Reference 9, pp. 235–258.
25. H. Endres, H. J. Keller, M. Megnamisi-Bèlombè, W. Moroni, H. Pritzkow, J. Weiss and R. Comès, Acta Cryst. **A32**, 954 (1976).
26. H. Endres, H. J. Keller, R. Martin and U. Traeger, Acta Cryst. **B35**, 2880 (1979).
27. J. S. Miller, J. Am. Chem. Soc. **96**, 7131 (1974).
28. D. Jerome, A. Mazaud, M. Ribault and K. Bechgaard, J. Phys. Lett. **41**, L95 (1980).
29. K. Bechgaard, K. Carneiro, M. Olsen, F. B. Rasmussen, C. S. Jacobsen, Phys. Rev. Lett. **46**, 852 (1981).