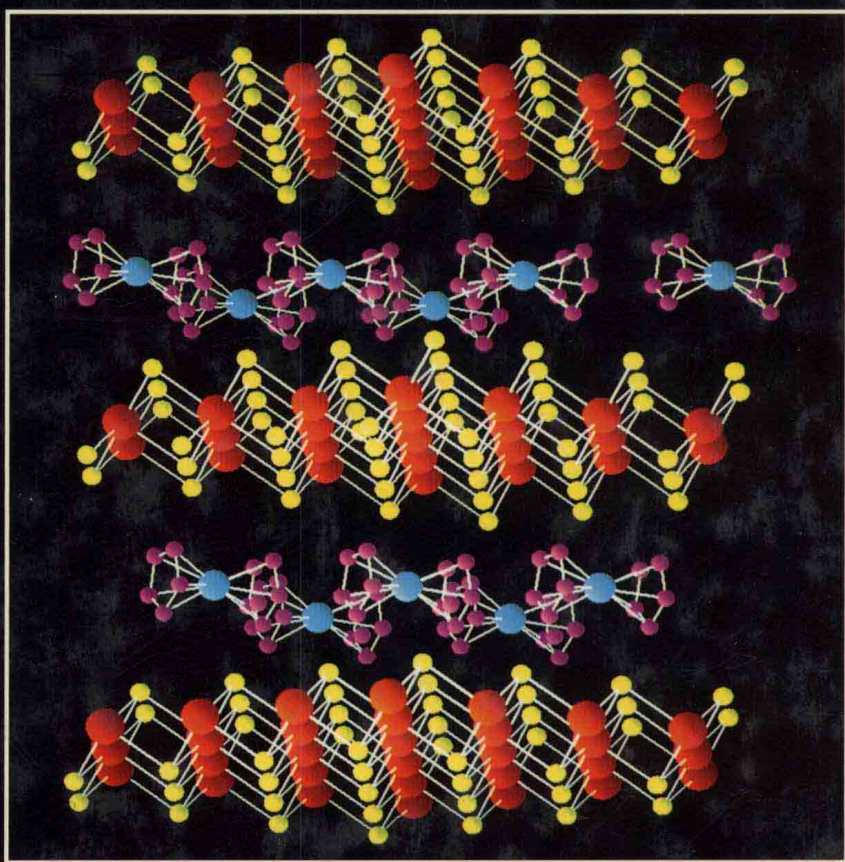


Inorganic Materials



Edited by
Duncan W Bruce and Dermot O'Hare

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A perspective view of the X-ray structure of $\text{SnS}_2\{\text{Co}(\eta\text{-C}_5\text{H}_5)_2\}_{0.3}$.

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Back cover illustration

The X-ray structure of $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$

(pbaOH = 2-hydroxy-1,3-propylenebis(oxamato))

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To our families, Sue, Ciarán, Anita, Katie and Annie

Preface

In recent years, Materials Chemistry has enjoyed something of a renaissance and expansion, although there are still few texts available which cover the area. This book then seeks to fill a part of that gap by considering some aspects of inorganic materials.

We have chosen a multi-author format in order to benefit from researchers who are active in their chosen fields and who can therefore give the best account of their subject. We have also used mainly younger authors as we felt that their energy, enthusiasm and relatively new entry in these areas would provide new perspectives. To try to do justice to the whole field of inorganic materials would have been impossible in a volume such as this, so we have emphasised discussions of the properties of molecular solids, as these provide the exciting possibility of controlling bulk properties by tuning molecular properties.

The book is intended to provide a well-referenced introduction to each subject, followed by an overview of the area and then concentrating on selected examples in order to emphasise best the materials under discussion. We feel that the authors have achieved this admirably and that the book will be useful for anyone wanting to start work in any of these areas, or requiring an overview of a particular field. As such, we hope that the book will be of some use in the final year of undergraduate courses, as well as to researchers in both academia and industry.

Readers may be interested to learn that the editing and production of this book have been achieved using AppleTM Macintosh computers running Microsoft WordTM, ChemDrawTM, Chem3DTM, Cricket GraphTM, KaleidagraphTM and MacDrawTM software.

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DWB

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1.1 BACKGROUND

Since the discovery of superconductivity in mercury by Kammerlingh-Onnes in 1911 until the early nineteen seventies, only elements or metal alloys were proven to exhibit this incredible property: namely that below a given temperature, called the critical temperature T_c , the material has zero resistivity. In 1973 the highest critical temperature, 25.5 K, was observed for the $[Nb_3Al_{0.8}Ge_{0.2}]$ alloy.

More recently, superconducting Nobel-prize winners based on copper oxides, such as $[\text{YBa}_2\text{Cu}_3\text{O}_{6+x}]$, have broken the 'wall of the liquid nitrogen temperature' ($T_c > 77 \text{ K}$).

Another family of superconductors, the Chevrel phases, discovered in the seventies, consists of ternary molybdenum chalcogenides, such as $[\text{PbMo}_6\text{S}_8]$ ($T_c = 15.2 \text{ K}$).

However, the first true molecular superconducting compounds were obtained in 1980 by Bechgaard, and were derived from a purely organic molecule, tetramethyltetraselenafulvalene, TMTSF. Clearly, the molecular inorganic chemists were challenged.

Gratifyingly, the first molecular inorganic superconductor, $[\text{TTF}][\text{Ni}(\text{dmit})_2]_2$ (TTF = tetrathiafulvalene; $\text{dmit}^{2-} = 1,3\text{-dithiol-2-thione-4,5-dithiolato}$) was obtained in 1986 in our group in Toulouse. The following chapter is devoted to this exciting, challenging, and finally successful, quest.

1.1.1 The KCP Complexes

The first episode of what could be called the 'Molecular Inorganic Superconductors Saga' was unconsciously written by Knop as early as 1842 [1]. He prepared 'kupferglänzenden' (copper-shining) crystals by oxidizing $\text{K}_2[\text{Pt}(\text{CN})_4]$ with chlorine or bromine, but could not fully characterise these crystals. Knop was not at all aware that his compound was the first 'Molecular Inorganic Conductor'.

In fact, if Levy in 1912 did suggest the presence of mixed valent states in these complexes [2], later called 'KCP' from the German 'kalium tetracyanoplatinat', more than a century passed before Krogmann clarified their actual stoichiometry in 1968; $\text{K}_2[\text{Pt}(\text{CN})_4\text{X}_{0.3}]\cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$), with all platinum atoms in the same non-integral oxidation state [3]. Their structure (Figure 1) was characterised by columns of $\text{Pt}(\text{CN})_4$ anions stacked along the direction perpendicular to the $\text{Pt}(\text{CN})_4$ plane, with Pt–Pt distances of 2.88 \AA , i.e. slightly longer than the Pt–Pt distance in platinum metal (2.77 \AA).

The suggestion made on the basis of these structural features (and, perhaps, their metallic lustre) that the KCP complexes might exhibit novel electrical properties was eventually confirmed by Zeller [4]: the room temperature conductivity along the stacking direction was $\approx 300 \text{ S cm}^{-1}$, with a large anisotropic ratio (the conductivity parallel to the Pt chains is 10^5 greater than the conductivity perpendicular to the chain direction), and the temperature dependence in the high temperature range is indeed consistent with a metallic band structure. In

these compounds metallic behaviour arose from electron delocalisation along overlapped platinum $3d_{z^2}$ -orbitals and from the formation of a partially-filled band induced by partial oxidation. Therefore, the KCP complexes could be described as the first 'One-dimensional Molecular Metals'.

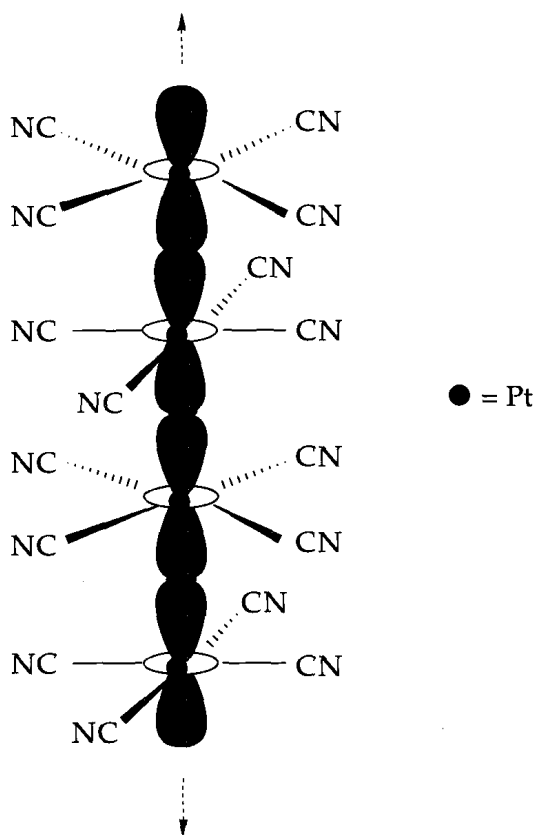


Figure 1 A chain of square-planar $\text{Pt}(\text{CN})_4$ groups in $\text{K}_2[\text{Pt}(\text{CN})_4]\text{X}_{0.3} \cdot n\text{H}_2\text{O}$ showing the overlapping of Pt d_{z^2} -orbitals (from [6])

Following these findings, the KCP complexes have been the subject of a large number of chemical modifications and physical and theoretical studies, which have been discussed in several review articles and books [5–8]. Whilst it appears from this extensive work that the KCP complexes may be used as textbook examples for illustrating how tight binding band theory may be successfully applied to one-dimensionally stacked molecular systems for rationalizing their physical behaviour, it

is also clear that, to date, neither the studied KCP-like complexes, nor their chemical modifications such as the related partially-oxidised bis(oxalato)platinate salts [8], retain their metallic characteristics down to low temperatures (not to mention becoming superconducting). When the temperature is decreased, all these systems undergo a lattice distortion accompanied by a metal-to-insulator transition that had been predicted by Peierls [9] as an inherent instability of a one-dimensional (1-D) metal.

1.1.2 The Organic Metals and Superconductors

Nevertheless, the fire of hope was still kept burning thanks to the suggestion by Little [10] that appropriate one-dimensional systems could fulfil the criteria for high temperature superconductivity.

Given the failure of the platinum chain compounds, an alternative route towards molecular superconductivity was offered by purely organic compounds. Shortly after the first synthesis of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ; Figure 2) in 1962 [11], it was discovered that many salts of this molecule were electrically conducting [12].

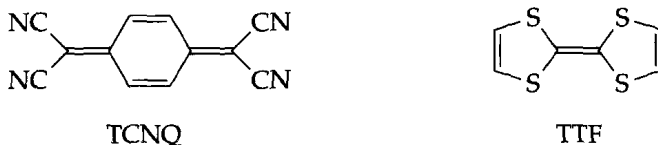


Figure 2 The TCNQ and TTF molecules

Starting in 1970, it was also discovered that another organic molecule, tetrathiafulvalene, (TTF) [13], could be halogenated to yield conducting salts [14]. However, the first 'Organic Metal' was only obtained in 1973, when these two molecules were combined in a 1:1 donor-acceptor compound [15]. In TTF.TCNQ, a partial charge transfer between separately stacked donor (TTF) and acceptor (TCNQ) molecules leads to two types of co-linear, one-dimensionally delocalised systems and the formation of partially-filled bands. A tremendous number of studies have been carried out on TTF.TCNQ and related compounds and several reviews have appeared [16–18].

In spite of this tremendous effort, up to 1980 none of the TTF.TCNQ-like organic metals retained their metallic characteristics down to low temperatures. As in the case of the KCP compounds, they all underwent a metal-to-insulator transition when the temperature was lowered.

In 1980, Bechgaard *et al.* used a molecule derived from TTF, tetramethyltetraselenafulvalene (TMTSF; Figure 3) to prepare radical salts of the type $(\text{TMTSF})_2\text{X}$, in which X was an inorganic cation such as PF_6^- , ClO_4^- , etc.

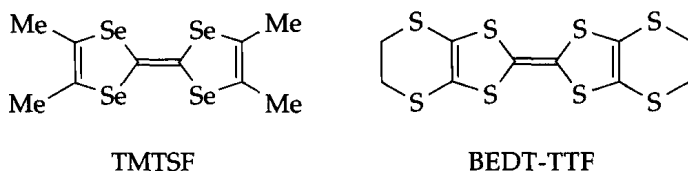


Figure 3 The TMTSF and BEDT-TTF molecules

At last, the holy grail was found: $(\text{TMTSF})_2\text{PF}_6$ was the first molecular compound to become superconducting under pressure [19] and $(\text{TMTSF})_2\text{ClO}_4$ was the first 'Molecular Superconductor' at ambient pressure [20]. Then, in 1984, another chemical modification of TTF, the bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), also yielded ambient pressure molecular superconductors of the type $(\text{BEDT-TTF})_2\text{X}$, in which X was I_3^- [21] or an inorganic cation such as $[\text{Cu}(\text{NCS})_2]^-$ [22] or $[\text{Cu}(\text{N}(\text{CN})_2)][\text{Y}]$ ($\text{Y} = \text{Cl}, \text{Br}$) [23, 24]. To date, the κ -phase of $(\text{BEDT-TTF})_2[\text{Cu}(\text{N}(\text{CN})_2)][\text{Cl}]$ exhibits the highest critical temperature T_c (12.8 K, 0.3 kbar) of any molecular superconductor [24].

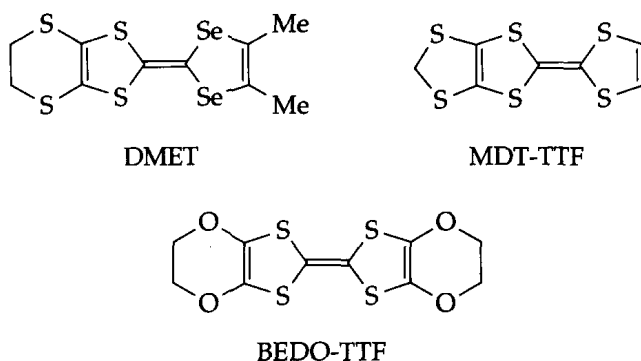


Figure 4 The DMET, MDT-TTF and BEDO-TTF molecules

Three additional modifications of TTF have also been used for the preparation of molecular superconductors, namely DMET (Figure 4) [25],