

Molecular Metals, a Summary

THE STATE OF THE ART

It is clear from the contributions to this issue of *Journal of Solid State Chemistry* that molecular metals, particularly organic molecular metals, are an exciting, active area of fundamental research in the general area of organic materials science. The early days of organic materials were dominated by engineering structural materials such as polyurethanes, epoxy resins, and other synthetic resins, but in the more recent past, they have indeed evolved with the discovery of organic molecular solids that exhibit properties normally associated with inorganic solids. These properties are metallic conductivity, superconductivity, ferromagnetism, and semiconductor device-derived properties. The latter include high charge carrier mobility, quantized Hall effect, and injection laser behavior [1]. A rather large branch of organic materials designed for the exploitation of semiconductor properties is the fluorescent conjugated polymers that, for the purposes of this issue of *Journal of Solid State Chemistry*, are not considered “molecular metals.” Instead, the emphasis is solely on donors such as TTF and TTF derivatives, as well as, with a couple of exceptions (C_{60} , perfluoroaromatics), on acceptors such as TCNQ, DCNQI, and the square planar transition metal sulfur and selenium complexes $M(\text{dmit})_2$ and $M(\text{mnt})_2$.

Molecular metals were established in the scientific community with two events, the discoveries of the Krogmann salts TTF-TCNQ. Strictly speaking, the former are actually polymers with Pt–Pt-bonded backbones (Pt–X–Pt for the Magnus green salts, related to the Krogmann solids). An interesting application of this polymer chain concept has recently appeared from a polymer science group at the ETH [2]. On the other hand, the square-planar transition metal complexes related to $M(\text{dmit})_2$ are more akin to molecular solids than to polymers.

Historically, the principal driving force behind molecular metals has been the pursuit of superconductivity. The main impetus arose from W. A. Little’s proposals of excitonic superconductivity nearly 4 decades ago [3] and the claim of Fröhlich superconductivity in TTF-TCNQ 30 years ago [4]. The pursuit of higher T_c in molecular superconductors and the coexistence of magnetic and metallic (superconducting) behavior are still the predominant driving forces in research dedicated to molecular materials. These aspects of molecular metals are essentially the subjects of

practically this entire issue of *Journal of Solid State Chemistry*.

One of the more outstanding features of these unusual molecular solids is the dimensionality of their structure and electronic character. This aspect was addressed expertly in this issue by J. M. Fabre. In the early days of molecular metals, low-dimensionality and molecular metals were synonymous. Since the Peierls distortion is a strong force that drives low-dimensional molecular metals to ground state insulators, many different avenues were taken to increase the dimensionality of these molecular solids. From a molecular design point of view, the idea was to increase intermolecular interactions by increasing the number of chalcogen atoms on the periphery of TTF. This idea worked up to a point and eventually led to the relatively high metal-to-superconductor transition temperatures observed with the ET salts, which, in turn, led to an explosion of research on molecular solids based on this molecule. For example, in this issue 11 of the 36 papers are based solely on ET materials and several more also involve this molecule as either magnetic materials or complex materials with inorganic solids. The advent of the fullerenes finally “solved” the quest for three-dimensionality, again with phenomenal results, culminating in high- T_c superconducting materials [5]. The developments concerning the unusual C_{60} molecular materials are addressed in this issue in the paper by S. Margadonna and K. Prassides.

From a physics point of view, low-dimensional metals with very low bandwidth are at the edge of instabilities and can give rise to a plethora of condensed matter phenomena such as charge density wave (CDW) and spin density wave (SDW) driven transitions. These solid-state phase transitions are all resistive but can be overcome with external influences such as pressure and high magnetic fields. In the metallic state, a number of interesting magnetoresistance phenomena have been recorded over the years, particularly in the tetramethyltetraselenafulvalene (TMTSF)X salts [6].

In addition to superconductivity, driving force in the development of molecular metals has been the possibility of magnetic ordering to produce ferromagnetic organic metals [7]. Before and since the advent of that first paper, a number of publications have appeared in this intriguing area [8]. In this issue, this and related phenomena, such as the coexistence of antiferromagnetism and metallic conductivity in an organic–inorganic molecular composite metal, as well as the coexistence of ferromagnetism and

conductivity and paramagnetism and conductivity and giant negative magnetoresistance in a molecular solid, are reported in a substantial number of papers in this issue.

THE FUTURE

The future of molecular metals is bright, indeed. A case in point is that of the conjugated polymers, where the academic research focus was in ever-increasing room-temperature conductivity and metallic behavior until the discovery of electroluminescence. This discovery catapulted these molecular materials onto the technology sector, eventually culminating in actual commercial devices and a Nobel Prize. I believe the future of molecular metals rests squarely with a dialog with technology; i.e., more effort should be dedicated to make a technological application possible.

The foundation for the future still rests with the *design and synthesis* of new systems but the *processing* (chemical engineering) will be much more relevant to the development of the whole field.

A step in the right direction was taken by the authors of two papers in this issue: in one paper, a joint Spanish–French group, headed by Fraxedas, reports the formation of thin-film TTF-TCNQ; in a second paper a French group, headed by Valade, reports formation of thin films and nanowires of TTF[Ni(dmit)₂]₂. This important Ni(dmit)₂ salt, of course, was discovered and studied extensively by the editor of this issue, Professor Patrick Cassoux. I further believe that the molecular metals based on the

transition metal square-planar chalcogen complexes will play a most important role in the development of this increasingly more important field of molecular materials.

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Patrick Cassoux
Guest Editor