

## Solid-state chemistry

## Novel molecular metals

Martin R. Bryce

THE scope of materials that display interesting electrical, magnetic and structural properties at very low temperatures has now been extended by Underhill and co-workers, who on page 547 of this issue<sup>1</sup> describe the first two-dimensional organometallic compound that exists in an integral oxidation state. The study of the synthesis and solid-state properties of such conducting two-dimensional systems will help to elucidate many fundamental phenomena of solid-state chemistry.

Most organic and organometallic solids are electrical insulators, but considerable attention has recently been focused on an ever-increasing number of these solids that exhibit high electrical conductivity and other properties typical of metals. This metallic behaviour is caused by extensive intermolecular overlap of systems rich in  $\pi$ -electrons along highly ordered stacks within the crystal. The materials are highly anisotropic and are termed quasi-one-dimensional molecular metals<sup>2,3</sup>.

Because of instabilities inherent in a one-dimensional electron system, metallic behaviour is almost invariably destroyed at low temperature by a Peierls transition when the materials become semiconducting or insulating. (This transition is analogous to the Jahn–Teller symmetry-breaking distortion in molecules.) A major goal of research on molecular metals is the stabilization of the metallic state at very low temperatures. The report by Underhill and colleagues of a new metal–dithiolenic complex with an inherently two-dimensional structure, a feature which suppresses the usual Peierls transition and

tion in molecular metals is a direct consequence of the one-dimensional nature of their crystal structures. The component molecules crystallize in an orientation such that their electronic states mix to form a continuous band along only one crystal axis. The highest energy level within the band that the electrons occupy is termed the Fermi level. At low temperatures, long-range order cannot be sustained and lattice distortions lead to the opening of a band gap at the Fermi level. When this occurs the conducting chain can be considered to stretch in one region and contract in another, so that the conducting electrons become localized with a filled electron band at a lower energy and an empty band at a higher energy. This transition usually occurs at a well-defined temperature (typically between 20 and 100 K) often when the component molecules of the conducting stack dimerize. Above this temperature electrons can be thermally excited across the Peierls gap and a uniformly spaced (metallic) stack is energetically preferred.

In contrast, for a two- or three-dimensional system, where there is also significant coupling between molecules in a plane perpendicular to the stacking axis, it is less favourable, or even impossible, for the lattice to rearrange and open a

band gap. The application of pressure to the sample is known to increase the strength of the two-dimensional interactions in TMTSF and BEDT–TTF salts<sup>4</sup>.

The discovery by Underhill and colleagues of a complex in an integral oxidation state that nonetheless displays metallic conductivity is also a significant advance. When a complex is in a non-integral oxidation state there is only partial charge on each anion. This means that energy levels will exist close to the Fermi level that are empty and available to receive the electrons required for conduction along the stack. This situation typically arises when there is full charge transfer between donor and acceptor molecules that crystallize in the ratio 1:2 or 2:3, or when there is only partial charge transfer from donor to acceptor that are present in a 1:1 ratio. Conversely, for a complex in an integral oxidation state there is a completely filled band and energy is needed to activate electrons into states where they will be available for conduction. Such materials are typically semiconductors or insulators. In simple terms, movement of electrons along the stack will now necessitate placing two electrons on the same acceptor, with the associated unfavourable coulombic repulsion between these two electrons. □

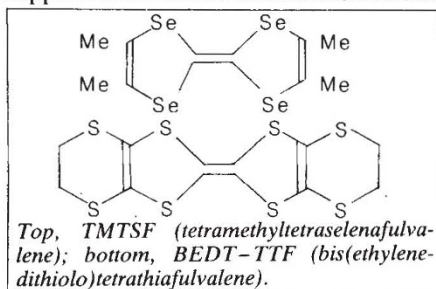
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## Pattern formation

## Form and diffusion

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stabilizes the metallic state down to 1.4 K under a pressure of 12 kbar, is therefore of considerable interest.

A significant degree of two-dimensional behaviour has been found previously in molecular metals which are salts of TMTSF and BEDT–TTF (see figure), where X-ray analysis reveals close interstacked selenium–selenium or sulphur–sulphur contacts<sup>4</sup>, but two-dimensionality is a new structural feature for highly conducting organometallic salts.

The physical basis of the Peierls transi-

THE question of how cells estimate their location within the body has preoccupied embryologists for the past century, but when posed by Stumpf<sup>1</sup> almost exactly 20 years ago, it seemed to have the beginnings of an answer. The concept of gradients, first explicitly propounded by T. H. Morgan, was entering a new phase of development, and since then it has become almost axiomatic to theories of pattern formation in insects. Yet for all that, direct evidence of the existence of gradients has remained tantalizingly elusive. The recent discovery<sup>2</sup> of the fruitfly (*Drosophila*) gene *caudal* (*cad*), whose transcripts form a concentration gradient in the early embryo, suggested that the search might at last have borne fruit. On page 537 of this issue<sup>3</sup>, Macdonald and Struhl report an extensive analysis that argues against a role for *cad* as a primary morphogen. In addition, the detailed characterization of primary determinants of polarity in

*Drosophila* by Nüsslein-Volhard and colleagues<sup>4,5</sup> suggests that a reassessment of the gradient paradigm is timely.

Since the beginning of this century, gradients have been invoked as determinants of polarity in a wide variety of organisms<sup>6</sup>. Analysis of polarity perturbations in insect segments had in particular provided support for this view. In the 1960s both Stumpf<sup>1</sup> and Lawrence<sup>7</sup> realized that the postulated gradients of “unknown diffusible substances”<sup>1</sup> could not only determine polarity, as Morgan had suggested as early as 1905, but also “that a particular level of the gradient might determine the pattern differentiated by cells”<sup>7</sup> at any given position. This concept was later embodied in Wolpert’s theory<sup>6</sup> of positional information, according to which cells in a morphogenetic field read the local concentration of a morphogen gradient, interpret the information and differentiate accordingly.

Although these authors had been con-