HUMPHRY DAVY LECTURE. Halides Magnetic, Halides Superconducting

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1 Electrochemistry and Davy

Among the most illustrious and productive of my predecessors as Director of the Royal Institution, Humphry Davy (1778—1829) was responsible for identifying and isolating more chemical elements than anyone else, before or since. In Group 1, Na and K, and all the Group 2 metals except Be first saw the light of day in the Laboratory at 21 Albemarle Street.[1] In addition, although he was not the first to isolate chlorine (an accolade that belongs to Schiele), it was Davy who first showed that it was an element. Likewise, while on the celebrated European tour which he made with his wife and young assistant Michael Faraday in 1812—1814, he used the analytical chemistry kit, which he always took on his travels, to identify a volatile purple solid extracted from seaweed as another element, iodine. Davy's credentials as a student of the halogens are therefore impeccable, and provide one reason for my choice of subject for a lecture bearing his name. Another is that the method for making many of the halides I am going to describe is also strongly associated with Davy, namely electrochemistry.

The Minutes of the Managers of the Royal Institution record that on July 8th 1808, Mr Davy (as he then was) laid before them the following proposal:

> A new path of Discovery having been opened in the agencies of the Electrical Battery of Volta, which promises to lead to the greatest improvements in Chemistry and Natural Philosophy, and the useful Arts connected with them, and the increase of the size of the Apparatus being necessary for pursuing it to its full extent, it is proposed to raise a fund by subscription, for constructing a powerful Battery, worthy of a National Establishment, and capable of promoting the great objects of Science.
>
> Already in other Countries, public and ample means have been provided for pursuing these investigations. They have had their origin in this Country, and it would be dishonourable to a nation so great, so powerful, and so rich, if, from the want of pecuniary resources, they should be completed abroad.
>
> An appeal to enlightened individuals on this subject can scarcely be made in vain. It is proposed that the instrument and apparatus be erected in the Laboratory of the Royal Institution, where it shall be employed in the advancement of this new department of Science.

Professor Day was born in 1938 in Kent and was educated at the local village primary school and nearby grammar school at Maidstone. He was an undergraduate at Wadham College, Oxford, of which he is now an Honorary Fellow. His doctoral research, carried out in Oxford and Geneva, initiated the modern day study of inorganic mixed valency compounds. From 1965 to 1988 he was successively Departmental Demonstrator, University Lecturer and Ad Hominem Professor of Solid State Chemistry at Oxford, and a Fellow of St. John's College. Elected Fellow of the Royal Society in 1986; in 1988 he became Assistant Director and in 1989 Director of the Institut Laue-Langevin, the European high flux neutron scattering centre in Grenoble. Since October 1991, he has been Director and Resident Professor of Chemistry, The Royal Institution, and Director of the Davy Faraday Research Laboratory.

The strands of his argument will be extremely familiar to anyone who writes, or assesses, research grant proposals today: first, Davy refers to successful feasibility experiments; second, he invokes the sophistication factor; third, he draws attention to the potential loss of Britain's leading position in the field to better funded groups in other countries, and finally he appeals to the good judgement of his interlocutors. I am pleased to say that his proposal was funded, and a number of copper–zinc batteries were built. They consisted of rectangular mahogany boxes lined with pitch, into which rows of bimetallic plates were slotted. The batteries were then connected together in series. The array of such batteries shown in the engraving in Figure 1 was almost certainly not completed in its entirety: then, as now, only partial funding was achieved!

Among the elements that Davy isolated by the electrolysis of molten salts was potassium. Noting its shining appearance, he realized that in spite of its low density it should be classified as a metal, and referred to it as a 'perfect conductor'. However, despite the fact that the resistance of potassium diminishes as the temperature is reduced, it does not become zero, even at the lowest temperatures. Hence, although Davy did not know it, the adjective 'perfect' was misplaced. It was almost one century later, in 1910, that the first truly 'perfect' conductor was discovered, in the form of another element, mercury, though the name given to the phenomenon of the complete loss of electrical resistance was in fact *super*conductivity. In what follows, I want to survey some recent work on halogen-containing compounds that exhibit this extraordinary property of superconductivity. As a complement, I will also consider another class of halides whose electronic ground state exemplifies another remarkable collective state of matter, namely ferromagnetism. In both cases the compounds concerned are synthesized by chemical methods that would not have appeared entirely alien to Sir Humphry Davy. The work described here concentrates mainly on the activities of my own research group.

2 Synthesis

2.1 Metallic and Superconducting Halide Salts

The most extensive class of halogen-containing salts that behave as metals or superconductors are based on the organo-sulfur compound bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), a relative of TTF, whose charge-transfer complexes were much studied during the 1970s. The first halide salt found to be superconducting was the tri-iodide $(\mathrm{BEDT\text{-}TTF})_2\mathrm{I}_3$, a compound which exists in two modifications, one with T_c of 1.3 K and the other of 8 K. The interest sparked by this discovery led to a widespread search for other salts exhibiting this unusual property.[2] To a chemist, the most obvious field to explore was that of other small linear tri-atomic anions, which includes not

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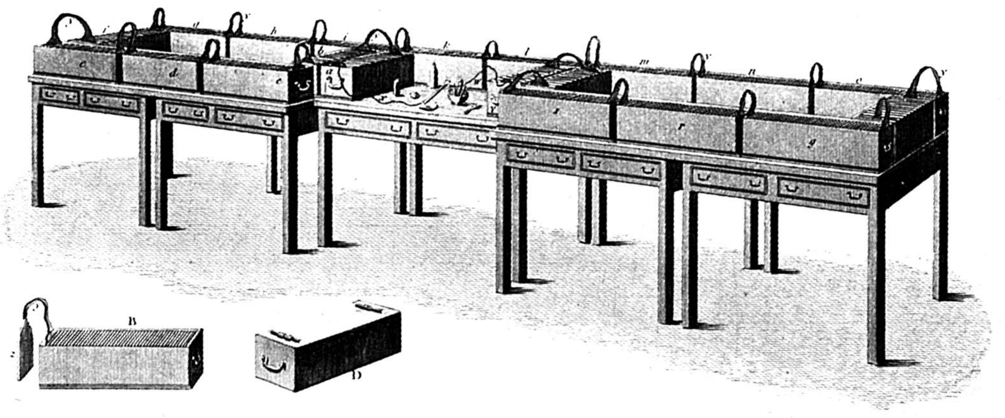

Figure 1 Batteries in the basement of the Royal Institution in the early nineteenth century.

only the interhalogens such as IBr_2^-, $IClBr^-$ *etc.* but anionic complexes of Group 11. Thus it was quickly found that (BEDT-TTF)$_2$AuI$_2$ is a superconductor ($T_c = 3$ K)[3] while the corresponding $AuBr_2$ salt is not.[4]

Nearly all the salts of the type (BEDT-TTF)$_n$X$_m$, where X is a mononegative anion, that have been prepared to date have been crystallized electrochemically. BEDT-TTF is oxidized in solution in a dipolar aprotic solvent such as CH_2Cl_2 or CH_3CN in the presence of a salt (usually tetra-n-butylammonium) of X^-. An alternative method of solubilizing X^-, used from time to time, has been to react a Group 1 salt with a cyclic polymer such as 18-crown-6. Sometimes it may be necessary to use mixed solvents, such as 10% CH_3CN: 90% CH_2Cl_2saturated with $[(CH_3)_4N]_2CuCl_4$ in the preparation of (BEDT-TTF)$_3$CuCl$_4$.H$_2$O. In any case the solvents are purified by distillation before use.

Crystal growth is best accomplished in a three-compartment cell, in which two glass frits inhibit diffusion of by-products formed at the cathode into the crystal growing compartment. Both electrodes are Pt wire: considerable experimentation with other shapes, and methods of surface preparation, have shown that this is the optimum configuration. Typical conditions (*e.g.* for the $CuCl_4$ salt just mentioned) might be a constant current of 2 μA for at least 10 days. Crystals prepared in this way are shown in Figure 2. Quite frequently, more than one phase crystallizes at the same time: for example, in addition to the hexagonal plates of (BEDT-TTF)$_3$CuCl$_4$.H$_2$O, multifacetted needles of (BEDT-TTF)$_2$CuCl$_4$ also form and can be separated by hand.[5]

In a few cases chemical oxidation of BEDT-TTF can lead to formation of charge-transfer salts. For example, when $CuCl_2.2H_2O$ in CH_3CN solution is placed in one arm of a U-tube which has a glass frit separating the two arms, and BEDT-TTF in tetrahydrofuran in the other, slow inter-diffusion of the reactants over several days produces square black plates of (BEDT-TTF)$_2$CuCl$_2$.[6] On the other hand, when $CHCl_3$ is used as solvent for the BEDT-TTF, another salt, (BEDT-TTF)$_2$CuCl$_3$ is obtained as brown microcrystals with a metallic reflection.

It is pertinent to ask: can binary halides of BEDT-TTF be prepared? In fact the first such were prepared inadvertently, both in Britain and Japan,[7] where synthesis of other salts was being attempted. In the former, a dibenzyldithiocarbamate salt was being used as supporting electrolyte and in the latter a tetrachloro-cobaltate(II) salt. In the former the solvent was CH_2Cl_2 which releases Cl^- through an electro-catalysed reaction while in the latter the solvent was benzonitrile and the chloride comes from the anion; in both cases the product was (BEDT-TTF)$_3$Cl$_2$.2H$_2$O. On drying the solvent and reagents more rigorously, no crystals were produced, but on adding a small drop of water to the cell, crystals began to grow. In fact, under the latter conditions no fewer than three distinct phases (BEDT-TTF)$_x$Cl$_2$(H$_2$O)$_y$ have been isolated with x:y of 3:2, 4:4, and 4:6. The structures and properties of these compounds are summarized later. Interestingly, a number of other hydrated BEDT-TTF salts have been identified, including the first-known water-containing compound that is superconducting at ambient pressure, (BEDT-TTF)$_2$Ag(CN)$_2$H$_2$O.

2.2 Ferromagnetic Halide Salts

The first ferromagnetic halide to be discovered was $CrBr_3$, which is synthesized from the elements in a sealed-tube reaction, crystals being subsequently grown by sublimation. A ternary fluoride K_2CuF_4, which has a T_c of 6.3 K, was closely studied by physicists in the 1970s, in part because large single crystals can be grown from the melt. Ferromagnetic ternary compounds A_2MX_4 of the heavier Group 17 elements appear to be confined to Cr^{II} and Cu^{II}, with the former showing distinctly higher T_c's but being more tricky to synthesize because they are unstable to oxidation and hydration.[8] Where A is a Group 1 element, crystals of the Cr compounds can be grown from the melt by the Bridgman method, though care is needed with the K salt, which is not congruently melting. The largest family of ferromagnetic A_2MX_4 compounds, however, is the one in which A = RNH_3, since one can then have M = Cr or Cu and X = Cl, Br, or (at least in solid solutions with Cl) I.[9] The group R can be varied widely, including not only n-alkyl but aromatic groups. Such compounds are made by simple reaction of stoichiometric quantities of AX and MX_2 in a dipolar non-aqueous solvent such as ethanol or glacial acetic acid. Whilst anhydrous $CuCl_2$ is easily prepared from the hydrate by heating it in a stream of HCl gas, this method is not so convenient in the case of $CrCl_2$. It is better to dissolve the stoichiometric quantity of Cr metal in the thoroughly deoxygenated solvent by bubbling HCl gas through it. To grow crystals of $(RNH_3)_2CrX_4$ we sealed saturated solutions in tubes and then cooled them very slowly.[10] Some crystals prepared in this way are shown in Figure 3.

3 Structure

Although they have quite different electronic ground states the structures of the superconducting and ferromagnetic halides we are discussing have two broad features in common: both are layer structures and both consist of alternating organic cations and inorganic anions.

3.1 Superconducting Halides

In common with the majority of organic charge-transfer salts, the most prominent feature in the crystal structures of many of the superconducting BEDT-TTF halide salts is the presence of stacks of near-planar donor molecules. The phrase 'near-planar' denotes the fact that the peripheral $-CH_2CH_2-$ moieties adopt a chair conformation. Consequently, at either end of a given BEDT-TTF molecule, these C$-$C single bonds may either be parallel or inclined at a nearly orthogonal angle to each other. In some phases, indeed, their orientations are disordered; for

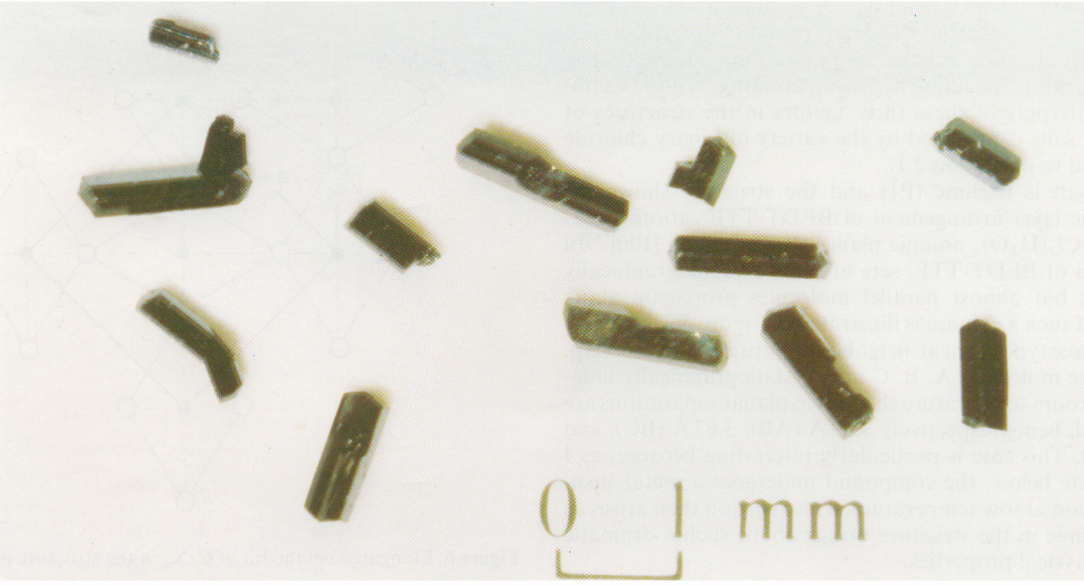

Figure 2 Crystals of α'-(BEDT-TTF)$_2$AuBr$_2$.

Figure 3 Crystals of $(CH_3NH_3)_2CrCl_4$.

example β-(BEDT-TTF)$_2$I$_3$ exists in two modifications, a disordered one with a superconducting T_c of 1.3 K and an ordered one obtained under pressure, which has T_c of 8 K.

Commonest among the BEDT-TTF conductors is the so-called β-phase, with 2:1 stoichiometry, a typical example of which is shown in Figure 4(a)[4]. This Figure emphasizes that, so far from being purely one-dimensional, and dominated by the stacking of the organic donors, segregation between the organic and inorganic components in the structure gives it more the character of a layer system. This character is further accentuated by the existence of a network of specific S···S interactions between molecules on neighbouring stacks. Such intermolecular contacts, shorter than the van der Waals radii, are quite a common feature in the structural chemistry of chalcogen-containing solids, including the elements themselves. An example of such a network, propagating in the plane of the donor molecules, is illustrated in Figure 4(b). In a simplified fashion, therefore, such structures may be thought of as containing two-dimensional 'blocks' of organic material interleaved by thinner layers consisting of the inorganic anions, a kind of chemically

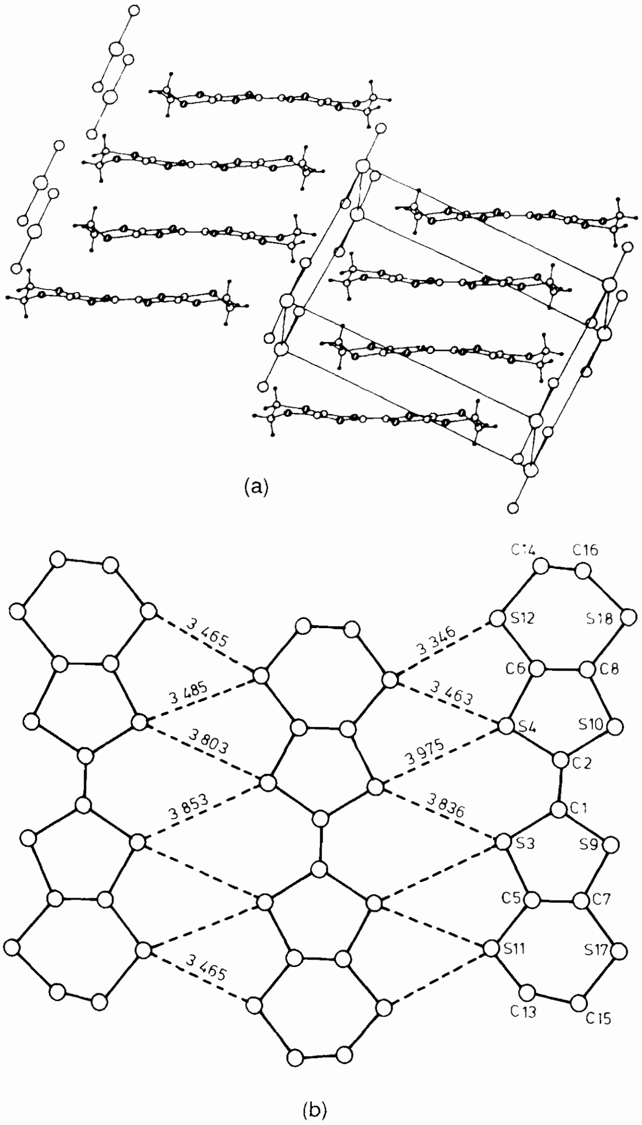

Figure 4 The crystal structure of β''-(BEDT-TTF)$_2$AuBr$_2$ showing (a) the alternating layers of organic and inorganic units, (b) the network of interstack S···S contacts.

constructed multilayer assembly Of course, such a global picture fails to do justice to the detail of individual structures, determined by chemical stoichiometry and the niceties of intermolecular packing, including hydrogen bonding A good example of the interplay of these three factors in the structures of BEDT-TTF salts is provided by the variety of binary chloride salts, referred to in Section 2 1

The 3 2 salt is triclinic (P1) and the structure shows the characteristic layer arrangement of BEDT-TTF cations interleaved with Cl$_2$(H$_2$O)$_2$ anionic planes stacked along [100][7] In each column of BEDT-TTF, sets of three crystallographically independent but almost parallel molecules propagate along [010] Part of such a column is illustrated in Figure 5, which also shows the three types of near-neighbour intermolecular overlap Although the molecules A, B, C are crystallographically independent, at room temperature their inter-planar separations are almost equal, being respectively 3 59 Å (AB), 3 67 Å (BC), and 3 68 Å (CA) This case is particularly interesting because, as I shall illustrate below, the compound undergoes a metal–insulator transition at low temperature The question then arises as to what change in the structure brings about such a dramatic change in physical properties

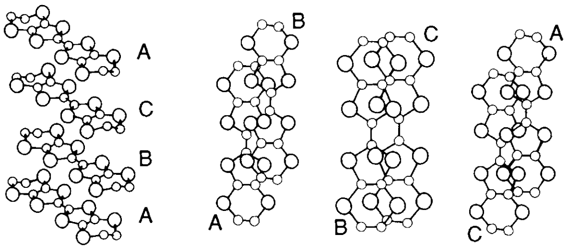

Figure 5 The stacks of organic cations in (BEDT TTF)$_3$Cl$_2$(H$_2$O)$_2$ Note the three independent molecules A B C

We attempted an answer to this question using single crystal neutron diffraction[11] Because of the small size of crystal available the results are not as precise as those obtained using *X*-rays at room temperature, but nevertheless the conclusion is clear From 300 down to 50 K the b-axis contracts 0 42 Å and the a-axis by 0 114 Å while the c-axis remains unchanged Structurally speaking, it turns out that the [010] contraction only affects one of the three intermolecular contacts along the stacks that between A and C, which contracts to 3 4 Å AB and BC are unaltered The shortest inter-stack S···S distances (3 3 Å) are not changed at low temperature though some of the longer distances contract from 3 47 to 3 3 Å

A second hydrated BEDT-TTF chloride phase, (BEDT-TTF)$_4$Cl$_2$ 6H$_2$O, also has a metal–insulator transition at low temperature, but unfortunately no structural data are available for the insulating phase At room temperature the compound is orthorhombic (Pcca), with the same alternation of cation stacks and anion layers observed in the 3 2 salt, but now with two rather than three types of cation–cation overlap along the stacks, *i e* ABBA[11]

Common to both salts is a set of H-bonds linking the Cl and H$_2$O in two dimensions The 3 2 salt contains what are effectively Cl$_2$(H$_2$O)$_2$ dimeric units, each pair of Cl being bridged by two Cl H−O−H Cl On the other hand the 4 2 salt has equally spaced Cl, each intersecting with a pair of H$_2$O, with a third water molecule H-bonded to the other two In all the other hydrated BEDT-TTF salts the water plays an important structural role in linking the anions together through H-bonds into layers

3.2 Ferromagnetic Halides

The anionic layers that comprise the structural elements in the ternary Cr^{II} and Cu^{II} halide ferromagnets are not built of molecular units, but consist of tetragonally elongated MCl$_6$ octahedra sharing corners The direction of elongation lies within the plane, and is orthogonal from one octahedron to the next An idealized view of such a layer is given in Figure 6 The cause of the elongation is Jahn–Teller distortion, universally found in high spin 3d^4 and 3d^9 compounds It is this distortion that ensures the orthogonality between the orbitals containing the unpaired electrons on neighbouring metal ion sites so necessary for achieving ferromagnetic exchange Taking the tetrachlorochromates(II) as specific examples, the Cr−Cl bond length perpendicular to the layer is 2 41 Å while in the plane one finds two Cr−Cl distances of 2 39 Å and 2 87 Å Because of the packing requirements of the organic cations that separate the [CrCl$_4^{2-}$]$_x$ layers, the latter not quite flat, but very slightly puckered (*e g* the Cr−Cl···Cr angle is 165°) The RHN$_3^+$ have their long axes perpendicular to the [CrCl$_4^{2-}$]$_x$ layers with the −NH$_3$ moiety lying within the pocket formed from four linked anion octahedra Owing to the lack of large enough single crystals, no neutron diffraction studies of the orientation of the −NH$_3$ have been reported, but in the related (RNH$_3$)$_2$MCl$_4$ (M = Mn, Cd) the amino-protons engage in weak H-bonding with both axial and equatorial Cl[13] As far as the R-groups are concerned, n-alkyl chains up to C$_{12}$H$_{25}$ have been incorporated separating the ferromagnetic layers by more than 30 Å Phenyl groups can be substituted in the chains, and there seems no reason why a wide variety of other functional groups should not be introduced, thus opening up the possibility of modulating the ferromagnetic properties by, for example mesomorphism or ferroelasticity

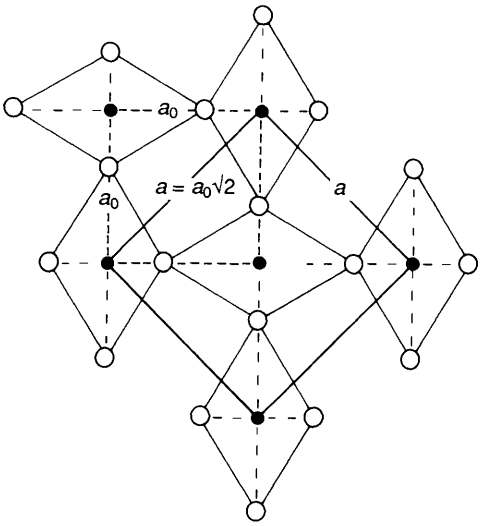

Figure 6 Elongated octahedra of CrX$_6$ in the structure of A CrX$_4$

4 Conductivity

The binary, and many of the complex halides of BEDT-TTF are metals, quite frequently becoming superconductors at low temperature While behaving as metallic conductors near room temperature, however, the two chloride salts whose structures were described above, undergo smooth transitions to an insulating state as the temperature is reduced[7] The behaviour of the 3 2 and 4 2 (6H$_2$O) salts is shown in Figure 7 The electrical resistance of a crystal, measured by 4-probes with d c or low frequency a c , at first goes down with decreasing temperature just as in an ordinary metal but in the range 150—100 K it first gradually and then quite steeply increases In the low temperature region the conductivity is activated, with an activation energy of about 0 1 eV The 4 2 salt behaves in quite a similar way, though the transition is spread out over an even wider temperature range[11]

Molecular crystals are quite soft, which is another way of saying that the intermolecular distances are easily modified by pressure This fact makes pressure a very useful variable for studying the properties of molecular conductors Whatever the

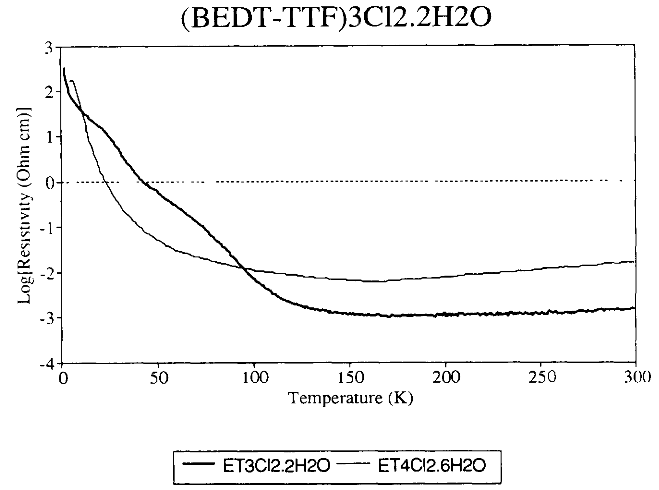

Figure 7 Temperature dependence of the electrical resistance of single crystals of $(BEDT\text{-}TTF)_3Cl_2(H_2O)_2$ and $(d_8\text{-}BEDT\text{-}TTF)_4Cl_2.6D_2O$.

details of the compressibility tensor in any specific compound, in general the effect of pressure is to increase the intermolecular orbital overlap and hence the electronic bandwidth. It also has the effect of 'stiffening' the lattice, increasing the frequency of the lattice modes. Assuming that vibrational–electronic coupling is the origin of the superconductivity in this class of materials, and not some other exotic mechanism, influencing the bandwidth and the lattice vibrational frequencies is sure to have an effect on the superconducting behaviour. That this is the case can be seen from Figure 8: hydrostatic pressure increases the normal state conductivity of $(BEDT\text{-}TTF)_2AuI_2$; in other words it becomes a 'better' metal.[14] Since superconductivity is associated with narrow bands, and a high electron density of states at the Fermi surface, we predict that those compounds that superconduct at ambient pressure should lose this property under pressure. In fact T_c of $(BEDT\text{-}TTF)_2AuI_2$ falls with pressure (Figure 9).

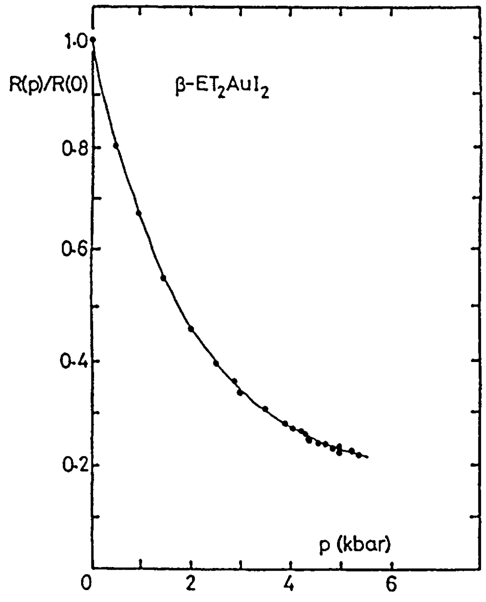

Figure 8 The effect of hydrostatic pressure on the room temperature conductivity of β-$(BEDT\text{-}TTF)_2AuI_2$.

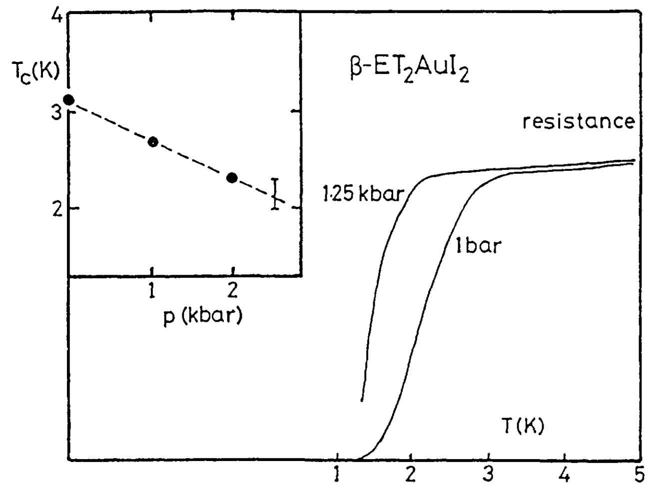

Figure 9 The effect of hydrostatic pressure on the superconducting transition in β-$(BEDT\text{-}TTF)_2AuI_2$.

Suppose, however, that we have a metal in which the orbital overlap at atmospheric pressure is such that it is close to the borderline between metallic and insulating behaviour. Applying pressure should increase the electronic bandwidth, reducing the tendency to localization. This is what happens in $(BEDT\text{-}TTF)_3Cl_2.2H_2O$. Under increasing pressure the metal–insulator transition moves progressively to lower temperature until above 14.5 kbar the insulating phase is completely suppressed.[15] The metal-to-insulator transition is then replaced by a metal-to-superconductor one (Figure 10). Applying pressure to the 4:2 salt likewise reduces its metal–insulator transition temperature, but at the highest pressure used so far (20 kbar) the transition temperature remains finite.

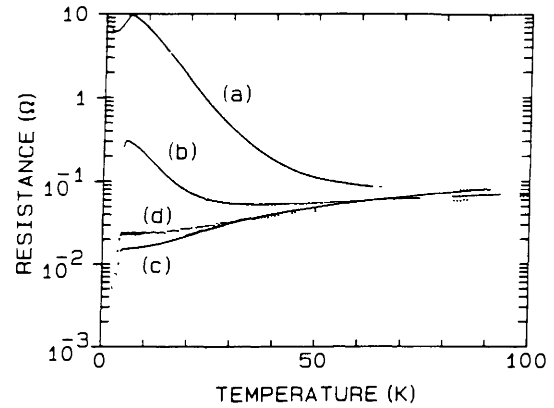

Figure 10 The effect of hydrostatic pressure on the electrical resistance of $(BEDT\text{-}TTF)_3Cl_2(H_2O)_2$. The metal-insulator transition is replaced by a metal–superconductor one, (a) 10, (b) 13, (c) 14.5, and (d) 15 kbar.

5 Magnetism

The ternary halide salts of Cr^{II} whose structures were described in Section 3.2 are in every sense ferromagnets: plots of the inverse susceptibility *versus* temperature indicate positive values of the Weiss constants in the range 55—77 K and they can also be fitted to the high temperature series expansion formula for two-dimensional easy-plane Heisenberg ferromagnets to yield estimates of the near-neighbour exchange constant ranging from 9—13 K.[16] Below the Curie temperatures, which vary from 59 K in $Rb_2CrCl_2I_2$ to 37 K in $(C_6H_5CH_2NH_3)CrCl_4$, the spontaneous magnetization increases smoothly to reach 80% of its saturation value of 4 BM per Cr at 6 K. They also exhibit classical, magnetic hysterisis (Figure 11), albeit with quite a low coersive field (130 G in the example shown).[17] As a spur to further chemical synthesis using more exotic molecular cations it is worth noting that T_c does not vary very strongly with the interlayer separation. For example, among the $(RNH_3)_2CrCl_4$, T_c is 42 K for $R = CH_3$ (interlayer spacing 9.4 Å) and 37 K for $R = C_6H_5CH_2$ (15.7 Å). For a given cation, the Curie tempera-

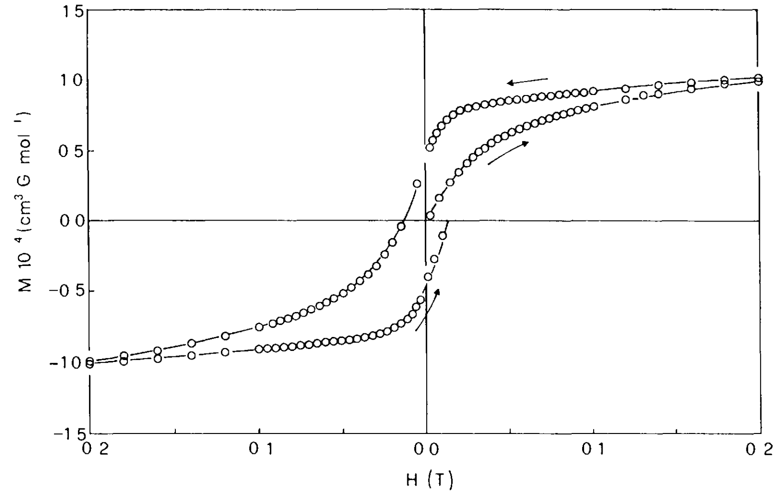

Figure 11 Magnetic hysterisis loop for $(C_6H_5CH_2NH_3)_2CrBr_{3.3}I_{0.7}$

ture goes up as Cl in the anionic layer is progressively replaced by Br and I, even though the interlayer spacing (*d*) also increases. Taking benzylammonium salts, for example, we find the following.[17]

	T_c/K	*d*/Å
$CrCl_4$	37	15.71
$CrCl_{0.7}Br_{3.3}$	49	16.10
$CrBr_{3.3}I_{0.7}$	51	16.15

Since the Cr–Cr distance also increases, the higher T_c in the heavier halide phases must be ascribed to increased metal–halogen convalency. It is a pity that so far no fluoride compounds have been reported.

6 Conductivity with Magnetism?

Given that superconductivity and ferromagnetism are supposed to be mutually exclusive states of matter from a theoretical point of view,[18] it is pertinent to ask whether molecular conductors can be made with magnetic moments embedded in their lattices. Charge-transfer salts of BEDT-TTF can be synthesized with many different anions, including transition-metal complexes. Unfortunately though the majority of these turn out to be insulators. Nevertheless their magnetic properties are interesting because localized magnetic moments are found associated with the organic cations as well as the inorganic anions.

A typical example is $(BEDT\text{-}TTF)_2FeCl_4$, whose magnetic properties, however, are dominated by the $S = 5/2$ state of the Fe^{III}.[19] Replacing the Fe^{III} by diamagnetic Ga^{III} makes apparent the unpaired spins on the organic cations.[20] Because the crystals contain stacks of BEDT-TTF, the moments on the latter interact, so the susceptibility varies with temperature like that of a one-dimensional antiferromagnet with a near-neighbour exchange constant of about 70 K. The $FeCl_4^-$ being molecular species, too, the exchange interactions between them are quite weak (*e.g.* Weiss constant 1—2 K).

A fascinating recent discovery is a halide charge-transfer salt behaving as a metallic conductor down to at least 400 mK, while at the same time containing localized magnetic moments.[21] The compound in question is $(BEDT\text{-}TTF)_3CuCl_4 \cdot H_2O$.[5] It has the customary organic–inorganic multilayer structure, with flattened tetrahedral $CuCl_4^{2-}$ linked into dimers by **H**-bonded water molecules. The organic array is unusual in not consisting of stacks but plane-to-plane dimers arranged orthogonally to one another: the so-called κ-phase structure – that of the highest T_c BEDT-TTF superconductors currently known, *e.g.* $(BEDT\text{-}TTF)_2Cu(SCN)_2$($T_c$ 11 K).[22] Even more intriguing is the fact that paramagnetic resonance signals can be seen both from the conduction electrons propagating in the organic layers and the Cu^{II} moments. Furthermore, there appears to be a weak but detectable interaction between them. Finally the temperature dependence of the spin susceptibility indicates a weak ferromagnetic interaction between the Cu, though no transition to a long range ordered state.[5] It is quite unusual to find a molecular metal which does not become either superconducting or insulating at low temperature: could it be that a transition to a superconducting state is prevented by the short range ferromagnetic correlations? For the present we have no sure answer, but one thing we can be quite certain about: when organic molecular cations are put together with inorganic halide-containing anions, the mix of conducting and magnetic behaviour will lead to strange and unexpected properties. A ferromagnetic molecular superconductor? Who knows? Humphry Davy would have found it fun.

Warmest thanks are due to my colleagues whose names appear in the references. The work described here has been partly supported by the SERC (UK), CNRS (France), CNR (Italy), and the British Council.

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