A supramolecular cation in an electrically conducting nickel dithiolate salt

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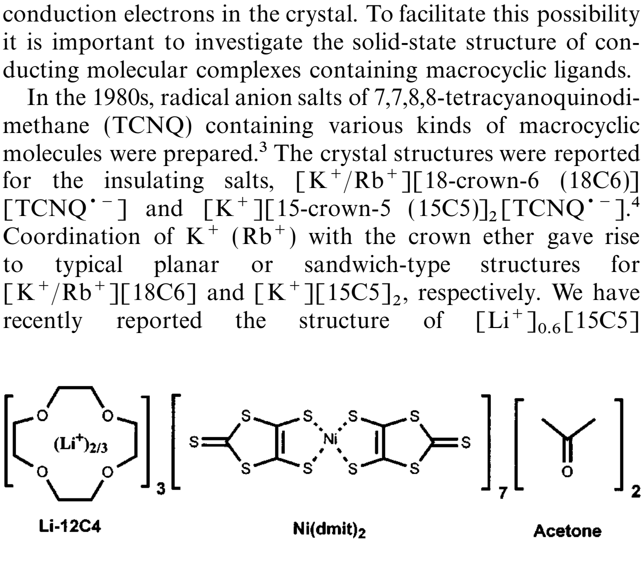
A novel dimeric penta-coordinated ion cavity of $[Li^+]_2$[12-crown-4-ether]$_3$ has been formed in the highly conducting $Ni(dmit)_2$ salt. This salt showed a room-temperature conductivity of 30 S cm^{-1} and exhibited a semiconductor–semiconductor phase transition on the application of pressure or on lowering the temperature.

The electronic, magnetic and optical properties of organic–inorganic hybrid molecular conductors have been studied widely.[1] Within this class of materials, the $[M(dmit)_2]$ complexes (M = Ni, Pd, Pt, Cu, Au; dmit = 2-thioxo-1,3-dithiol-4,5-dithiolate) have provided a number of organic metals or superconductors through the formation of electron-conducting molecular columns or layers in the solid state.[1a] In the molecular conductors of the type $[C^+][M(dmit)_2]_x$ ($x > 1$, C^+ denotes a closed shell monovalent cation) salts, the non-integral stoichiometry involving the counter cation compensates for the partially filled conduction band.

Macrocyclic compounds exhibit many characteristic properties, *e.g.* selective capture of ions and transport of ions through artificial or natural membranes.[2] In the solid state, the cavity within the macrocycle will offer an environment in which ions can be isolated from the chemical environment outside the macrocycle and in some cases the ions may have freedom to move between cavities in the solid state.

We have been interested in synthesising materials which can provide a cavity for counter ions in highly conducting molecular solids. Counter ions exert a strong influence on the conduction electrons through the formation of a potential field. Control of the arrangement and motion of ions in and between the cavities could provide new possibilities for regulating the conduction electrons in the crystal. To facilitate this possibility it is important to investigate the solid-state structure of conducting molecular complexes containing macrocyclic ligands.

In the 1980s, radical anion salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) containing various kinds of macrocyclic molecules were prepared.[3] The crystal structures were reported for the insulating salts, $[K^+/Rb^+]$[18-crown-6 (18C6)] $[TCNQ^{\bullet -}]$ and $[K^+]$[15-crown-5 (15C5)]$_2[TCNQ^{\bullet -}]$.[4] Coordination of K^+ (Rb^+) with the crown ether gave rise to typical planar or sandwich-type structures for $[K^+/Rb^+]$[18C6] and $[K^+][15C5]_2$, respectively. We have recently reported the structure of $[Li^+]_{0.6}$[15C5] $[Ni(dmit)_2]_2 \cdot 2H_2O$[5] and $[NH_4^+][18C6][Ni(dmit)_2]_3$,[6] which contain regular stacks of 15C5 macrocyclic molecules arranged parallel to the electron conduction path formed by the $[Ni(dmit)_2]$ ions, and NH_4^+ ions completely included at the centre of 18C6 to form supramolecular cations, respectively. We have now studied the structure and properties of the material with $[Li^+]$[12-crown-4(12C4)] as the counter cation. The resulting material contains a complex supramolecular entity involving dimeric penta-coordinated ion cavities situated between the electrically conducting $[Ni(dmit)_2]$ sheets.



The electrocrystallisation of $[NBu_4^+]$ $[Ni(dmit)_2^-]$ with a mixture of lithium tetrafluoroborate and 12C4 in acetonitrile–acetone (1:1) solution for two weeks at a constant current (1 μA) gave black single crystals with typical dimensions of $1.0 \times 0.4 \times 0.1$ mm^3. Elemental analysis indicated a composition of $[Li^+]_2[12C4]_3[Ni(dmit)_2]_7 \cdot 2Me_2CO$, $C_{72}H_{60}O_{14}S_{70}Ni_7Li_2$ (Calc.: C, 22.65; H, 1.57; N, 0.00%. Found: C, 22.87; H, 1.65; N, 0.00%). X-Ray crystal structural analysis also supports this composition.† The broad absorption band ascribable to the intermolecular transition from monovalent $[Ni(dmit)_2^-]$ to neutral $[Ni(dmit)_2^0]$ was observed with the absorption maximum at 0.21 eV.[7] Electrical resistivities were measured by a standard dc four-probe method using gold paste (Tokuriki 8560) to connect the gold wire (10 μm) to the crystal. Conductivity measurements under high pressure were carried out using a cramp cell with the pressure medium (dufni oil, Idemitu 7573).[8]

The salt showed a high electrical conductivity of 30 S cm^{-1} at room temperature (σ_{RT}). The σ_{RT} value is enhanced by about two orders of magnitude compared with $[Li^+]$ $[Ni(dmit)_2]_2 \cdot 2MeCN$ ($\sigma_{RT} = 0.5$ S cm^{-1}).[1a] The large molecular polarizability of the Li^+–macrocyclic supramolecular cation in contrast to the bare Li^+ present in $[Li^+][Ni(dmit)_2]_2 \cdot 2MeCN$ could be one of the reasons for the high σ_{RT} value. The temperature dependence of the conductivity at 1 bar showed semiconducting behaviour (Fig. 1). A transition is observed at around 230 K which separates two

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† *Crystal data*: $C_{72}H_{60}O_{14}S_{70}Ni_7Li_2$, $M = 3818.12$, crystal dimensions $0.5 \times 0.3 \times 0.1$ mm^3. Mac Science MXC18 diffractometer, Mo-Kα radiation ($\lambda = 0.710\,73$ Å), triclinic, space group $P\bar{1}$ (no. 2), $a = 9.075(4)$, $b = 18.370(5)$, $c = 20.677(5)$ Å. $\alpha = 91.376(21)$, $\beta = 93.829(28)$, $\gamma = 103.857(29)^\circ$. $U = 3336(2)$ Å^3. $T = 298$ K, $Z = 1$, $D_c = 1.904$ g cm^{-3}, $F(000) = 1926$, μ(Mo-Kα) 12.044 cm^{-1}. Lorentz, polarisation and absorption corrections applied, 16 887 reflections measured, 11 860 independent reflections, 7698 reflections with $I > 3.00\sigma(l)$ used in refinement. Calculations were performed using the Crystan-GM crystallographic software packages with refinements based on *F*. Weighting scheme employed: $w = 1/\sigma^2(F_o)$. Solution by direct methods; non-hydrogen atoms refined anisotropically, and no refinement of hydrogen atoms. $(\Delta\rho)_{max} = 1.09$ e Å^{-3}, $(\Delta\rho)_{min} = -1.33$ e Å^{-3}, $R = 0.0757$, $R' = 0.0753$. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/26.

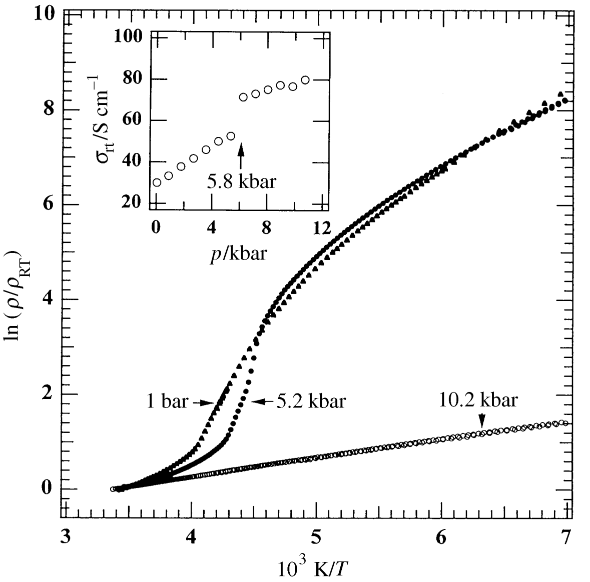

Fig. 1 Electrical conductivity of $[Li^+]_2[12C4]_3[Ni(dmit)_2]_7 \cdot 2Me_2CO$. Logarithmic resistivities normalised by the room-temperature value (ρ/ρ_{RT}) *vs.* inverse temperature (T^{-1}) at 1 bar (△), 5.2 (●) and 10.2 (○) kbar. Inset shows the pressure (p) dependence of conductivity at room temperature (σ_{RT}), and the jump of σ_{RT} is indicated by an arrow.

semiconducting phases denoted as the α (>230 K) and β phase (<230 K). The activation energy (E_a) of the α phase (0.10 eV) was lower than that of the β phase (0.17 eV). The conduction behaviour at 5.2 kbar was almost the same as that at 1 bar with E_a values of 0.09 and 0.15 eV for the α and β phase, respectively. However, the temperature-dependent conductivity at 10.2 kbar showed no evidence of a transition, with a linear Arrhenius plot over the whole temperature range with E_a = 0.07 eV.

An anomaly was also observed in the pressure dependence of σ_{RT}. Application of pressure increased σ_{RT} up to 80 S cm^{-1} at 10.2 kbar with a jump at 5.8 kbar (Fig. 1 inset). The α phase changes to a γ phase above 5.8 kbar. It is not clear at present whether this high-pressure γ phase is identical to the β phase.

Fig. 2(*a*) shows a projection of the unit cell viewed along the *b* axis. Four $[Ni(dmit)_2]$ (A–D), two 12C4 (E and F), one acetone molecule and the Li^+ ion are crystallographically independent, and one $[Ni(dmit)_2]$ (A) and one 12C4 (F) molecule are located on the centre of inversion. The segregated stacks of $[Ni(dmit)_2]$ and 12C4 molecules account for the observed optical properties and the high conductivity. The stacking mode in the $[Ni(dmit)_2]$ column is not uniform, which is one of the main reasons for the observed semiconducting nature of this salt, regardless of the high σ_{RT} value. The 12C4 molecules which are located in the *ab* plane in the interlayer space between $[Ni(dmit)_2]$ columns form an ion cavity which includes the Li^+.

Fig. 2(*b*) illustrates the $[Ni(dmit)_2]$ arrangements in the conducting layer viewed along the long axis of $[Ni(dmit)_2]$. The overlap integrals (10^{-3} t) were obtained from the extended Hückel molecular orbital calculations of the LUMO of each $[Ni(dmit)_2]$.[9] The $[Ni(dmit)_2]$ column elongates in the $2a-b$ direction in the stacking order A–B–C–D–D′–C′–B′–A′ (the primes indicate molecules generated by inversion centres). The mean interplanar distances (absolute t) between A–B, B–C, C–D and D–D′ in the stack are 3.21 (t_1 = 15.5), 3.78 (t_2 = 1.8), 3.60 (t_3 = 1.9) and 3.57 Å (t_4 = 0.7), respectively.

The overlap modes of A–B and C–D are metal-over-metal type, while those of B–C and D–D′ are of the metal-over-ring type. Owing to the b_{2u} symmetry of the LUMO of the $[Ni(dmit)_2]$ molecule, the effective overlap of the molecular orbitals in the later case is much smaller than in the former.

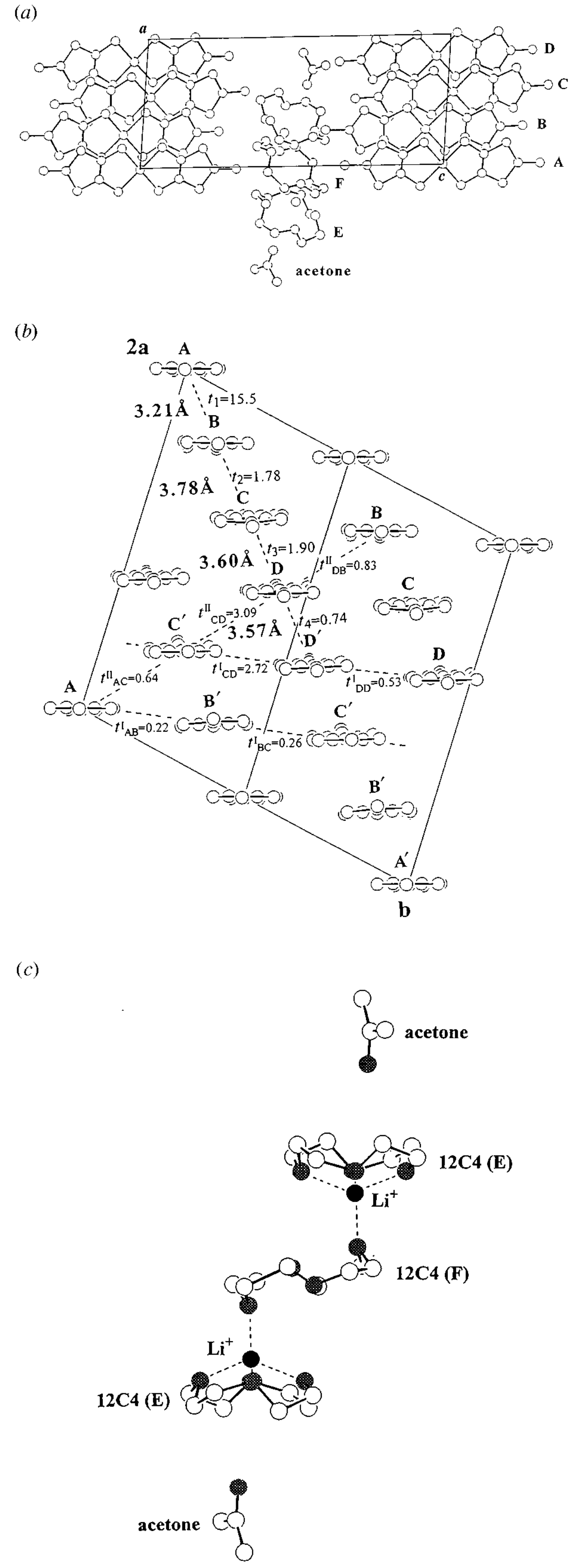

Fig. 2 Crystal structure of $[Li^+]_2[12C4]_3[Ni(dmit)_2]_7 \cdot 2Me_2CO$. (*a*) Packing motif in the unit cell viewed along the *b* axis. (*b*) Stacking mode of $Ni(dmit)_2$ layer viewed along the long axis of $Ni(dmit)_2$. The molecules A–D are crystallographically independent of each other. The mean interplanar distances of the $Ni(dmit)_2$ planes and the transfer integral (10^{-3} t) are indicated. (*c*) Fundamental structure of the ion cavity with dimeric pentacoordinated Li^+. The oxygen atoms are shaded, and the dashed lines indicate the $Li^+ \cdots O$ contact.

Within the column, the close overlap of A–B enhances the t_1 interaction, while the elongated mean interplanar distance of B–C decreases t_2. Also, the overlaps at C–D and D–D′ are decreased due to the symmetry of the LUMO. Thus, the column is composed of tightly bonded triads (B–A–B′) and loosely interacting molecules C and D.

The network of sulfur–sulfur interatomic contacts extends in the *ab* plane, through side-by-side interactions. Two types of side-by-side networks, I and II, indicated by transfer integrals t^{I} and t^{II}, respectively, extend in the *ab* plane. The absolute *t* values in the I and II networks are 0.22 ($t^{\mathrm{I}}{}_{\mathrm{AB}}$), 0.26 ($t^{\mathrm{I}}{}_{\mathrm{BC}}$), 2.72 ($t^{\mathrm{I}}{}_{\mathrm{CD}}$) and 0.53 ($t^{\mathrm{I}}{}_{\mathrm{DD}}$) for I and 0.64 ($t^{\mathrm{II}}{}_{\mathrm{AC}}$), 3.09 ($t^{\mathrm{II}}{}_{\mathrm{CD}}$) and 0.83 ($t^{\mathrm{II}}{}_{\mathrm{DB}}$) for II. The strong overlaps ($t^{\mathrm{I}}{}_{\mathrm{CD}}$ and $t^{\mathrm{II}}{}_{\mathrm{CD}}$) form the cyclic tetrad of C–D′–C′–D. The electron-conducting layer in the *ab* plane is composed of two units of the tightly connected triad B–A–B′ and cyclic tetrad C–D′–C′–D, and the transfer of a conduction electron between a triad and a tetrad is possible through the weak interactions t_2 and t_3.

The 12C4, acetone molecules and Li^+ ions form the 12C4 (E)–Li^+–12C4 (F)–Li^+–12C4 (E) structure [Fig. 2(*c*)]. A careful examination of the differential Fourier map showed no evidence of another Li^+ ion in the cavity of the 12C4 (F) molecule. The coordination sphere around the Li^+ ion consists of four basal oxygen atoms of 12C4 (E) and an apical one of 12C4 (F) resulting in the pentagonal oxygen coordinated nature of Li^+ ion. Similar penta-coordination of Li^+ by four basal oxygen of 12C4 and one apical nitrogen of bis(trimethylsilyl)amide and thiocyanate have been reported.[10] Two symmetrical oxygens of 12C4 (F) act as a spacer unit connecting two penta-coordination spheres. The distances between the Li^+ and the oxygen atoms of 12C4 (E) are 1.986, 2.051, 2.072 and 2.085 Å, which are longer than that of the apical oxygen (1.939 Å). The average $\mathrm{Li}^+\cdots\mathrm{O}$ distance (2.027 Å) is shorter than the sum of the van der Waals radius of oxygen and the ion radius of Li^+ (2.12 Å) or of typical $\mathrm{Li}^+\cdots\mathrm{O}$ distances for penta-coordination geometry (2.06 Å).[11] These results indicate that the Li^+ ion is tightly coordinated by five oxygens of the 12C4 cavity. The acetone molecule on the 12C4 (E) molecule isolates the ion cavities of 12C4 molecules from each other. The dimeric penta-coordinated 12C4 units are arranged along a nearly perpendicular direction to the stacking axis of $[\mathrm{Ni(dmit)_2}]$ or the same direction to the side-by-side interaction of II. There are no interatomic contacts shorter than the sum of van der Waals radii between $[\mathrm{Ni(dmit)_2}]$ and 12C4 layers. The dimeric penta-coordinated unit and acetone exist at the neighbouring spaces of the cyclic C–D′–C′–D tetrad and B–A–B′ triad, respectively.

Studies using other crown ethers and cations are now in progress to create various types of ion cavities in the conducting crystals.

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