

Unique structural topologies involving metal–metal and metal–sulfur interactions: salts of $[\text{Ni}(\text{C}_3\text{S}_5)_2]^{x-}$ with *cis-anti-cis*-dicyclohexyl-18-crown-6 complexed counter ions

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Preparation by electrocrystallisation has been carried out for the salts $[\text{Rb}(\text{anti-dchyl-18c6})]_2[\text{Ni}(\text{dmit})_2]$ **1**, $[\text{Rb}(\text{anti-dchyl-18c6})][\text{Ni}(\text{dmit})_2]$ **2**, $[\text{Cs}(\text{anti-dchyl-18c6})]_2[\text{Ni}(\text{dmit})_2]$ **3** and $[\text{Cs}(\text{anti-dchyl-18c6})_{1.5}][\text{Ni}(\text{dmit})_2]_6$ **4** (*anti-dchyl-18c6* = *cis-anti-cis*-dicyclohexyl-18-crown-6, *dmit* = C_3S_5). Salts **1** and **3** involve the planar dianionic nickel complex sandwiched by two metal–crown units. This leads to short $\text{Rb}^+ \cdots \text{Ni}$ and $\text{Rb}^+ \cdots \text{S}$ interactions in **1** and the shortest recorded $\text{Cs}^+ \cdots \text{Ni}$ distance of 3.47 Å in **3**, presumably stabilised by the four surrounding S atoms at 3.73–4.44 Å. DFT calculations on the dianionic salts **1** and **3** indicate an essentially electrostatic interaction between the $[\text{Ni}(\text{dmit})_2]^{2-}$ complex and the Rb^+ or Cs^+ ion and show frontier orbitals qualitatively similar to those previously derived from EHMO calculations on molecular conductors containing $[\text{Ni}(\text{dmit})_2]$. Salt **2** consists of non-stacked nickel complexes arranged in chains linked by $\text{S} \cdots \text{Rb}^+$ interactions through the terminal sulfurs with the Rb^+ ion placed exactly within the plane of the crown oxygens. Magnetic susceptibility measurement indicated weak antiferromagnetic interactions. Salt **4** shows a 2-D sheet of nickel complexes stacked in a herringbone arrangement separated by layers of counter ions complexed by the crowns in a disordered manner with the anion : cation ratio of 6 : 1 uniquely high among $[\text{Ni}(\text{dmit})_2]^{x-}$ salts. Salt **4** displays semiconductor behaviour with $\sigma_{\text{RT}} = 10^{-2} \text{ S cm}^{-1}$.

Introduction

Salts of $[\text{Ni}(\text{dmit})_2]^{x-}$ (Fig. 1) have been widely studied due to their ability to form molecular conductors and superconductors through the formation of intermolecular interactions in the crystalline phase combined with a flexibility in oxidation state that allows the partial band filling required for metal-like conductivity.^{1,2} Studies of such salts and those of related multi-sulfur organic species based on tetrathiafulvalene³ have involved systematic variation of the counter ions in order to change intermolecular interactions and hence the resultant conducting and magnetic properties. More recently, however, it has been recognised that the use of functional counter ions offers the opportunity to prepare hybrid species that can combine high conductivity with additional properties such as localised unpaired spins.⁴

In this context, studies have been undertaken using crown-ether complexed alkali metals as counter ions in molecular conductors and this has led to the observation of combined electronic and ionic conductivity in the salt $[\text{Li}_{0.6}(\text{15-crown-5})][\text{Ni}(\text{dmit})_2]_5$ and related salts.⁶ Such species provide model structures for mixed conductors of importance in applications such as fuel cells and batteries, and provide the opportunity to study electronic conductivity in the presence of mobile counter ions. In addition, crown ethers have been greatly investigated as components of supramolecular assemblies, where the role of the crowns in the preparation of novel crystal architectures and complexation modes is pursued.⁷ In the case of molecular conductors, where subtle changes in intermolecular interactions can have a profound influence on materials properties, crown ethers offer a highly versatile component for the preparation of novel structural topologies.

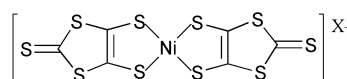


Fig. 1 $[\text{Ni}(\text{dmit})_2]^{x-}$.

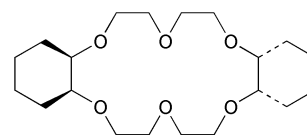


Fig. 2 *cis-anti-cis*-Dicyclohexyl-18-crown-6.

Previous studies involving molecular conductors have focused largely on unsubstituted crowns^{5,6,8} but we have recently shown that incorporation of the substituted crown dicyclohexyl-18-crown-6 can give rise to unusual $[\text{Ni}(\text{dmit})_2]^{x-}$ salts.⁹ In this context, we report the preparation, structures and properties of four $[\text{Ni}(\text{dmit})_2]^{x-}$ salts incorporating *cis-anti-cis*-dicyclohexyl-18-crown-6 (Fig. 2, hereafter referred to as *anti-dchyl-18c6*) and Cs^+ or Rb^+ counter ions. These species show structures and features not previously observed within the family of $[\text{Ni}(\text{dmit})_2]^{x-}$ salts despite intensive study of these over the last two decades. These include short $\text{Ni} \cdots \text{Cs}^+$ and $\text{Ni} \cdots \text{Rb}^+$ distances, non-stacked $[\text{Ni}(\text{dmit})_2]^{x-}$ species interacting with Rb^+ *via* terminal sulfurs, a 1 : 6 ratio salt and crystallisation by reduction at an anode.

Results and discussion

Preparation

The salts **1**, **2**, **3** and **4** were prepared in an H-shaped cell

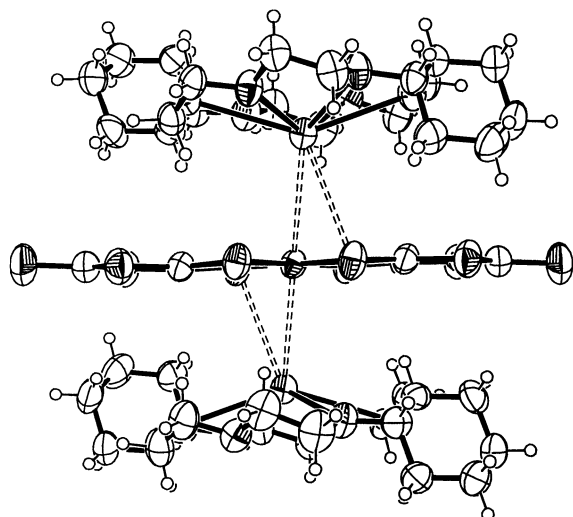


Fig. 3 Crystal structure of $[\text{Rb}(\text{anti-dchyl-18c6})]_2[\text{Ni}(\text{dmit})_2]$ **1** viewed along the short axis of $[\text{Ni}(\text{dmit})_2]^{2-}$.

with the two compartments separated by a porous glass frit. $[\text{NBu}_4][\text{Ni}(\text{dmit})_2]$ was placed in the anode compartment and the crown plus MClO_4 ($\text{M} = \text{Rb}$ or Cs) in the cathode compartment to encourage slow growth associated with diffusion of these species through the frit. This method, in addition to controlled growth of the conducting salt **4**, led to both the dianionic salts **1** and **3** by reduction of the $[\text{Ni}(\text{dmit})_2]^-$ in the cathode compartment and crystallisation with the crown complexed counter ion. Anodic oxidation of $[\text{Ni}(\text{dmit})_2]^-$ is the method normally applied¹ for preparation of conducting salts of $[\text{Ni}(\text{dmit})_2]^{+}$ and is exemplified here in the preparation of **4**. Cathodic reduction to form salts of $[\text{Ni}(\text{dmit})_2]^{2-}$ is not normally employed as a crystallisation method and thus preparation of **1** and **3** is unusual. Formation of the monoanionic salt **2** involved no redox step and is believed to have occurred simply by slow interdiffusion of the components of the salt from the different compartments. This was confirmed by the preparation of **2** by rapid mixing of the component solutions and standing for several days whereupon crystals of **2** formed.

Structures

[Rb(anti-dchyl-18c6)]₂[Ni(dmit)₂] 1. This crystallised in the space group $P2_1/c$ and consists of a sandwich-like arrangement, with the Ni atom on a centre of inversion and $[\text{Ni}(\text{dmit})_2]^{2-}$ complexes surrounded above and below by crown ether-complexed Rb^+ ions (Fig. 3). The Rb^+ ion is complexed by the crown oxygen atoms at distances 2.861–3.177 Å and lies 1.0178 Å towards the metal complex out of a plane defined by the six oxygen atoms. The rms deviation of the oxygen atoms from this plane is 0.1249 Å. The Rb^+ lies 3.3037 Å above the plane of the $[\text{Ni}(\text{dmit})_2]^{2-}$ unit and the shortest contact is with one of the metal coordinated sulfur atoms at 3.553 Å, with short contacts also with the Ni (3.600 Å) and the *cis* sulfur on the other dmit ligand. Thus the Rb^+ ions appear to be positioned above and below the plane of the metal complex in an asymmetric manner with respect to the position of the ligand donor atoms, stabilised by contacts with these electron rich sulfur atoms. This appears to influence the coordination of the sulfur atoms within the metal complex as these show values of 2.178 and 2.194 Å with the former for the S closest to the Rb^+ centre.

[Rb(anti-dchyl-18c6)][Ni(dmit)₂] 2. This crystallised in the space group $P2_1/n$ and consists of chains of $[\text{Ni}(\text{dmit})_2]^-$ and Rb^+ running along the *c* axis (Fig. 4). The metal complexes are linked *via* interaction of the terminal sulfur atoms to the Rb^+ ions at a distance of 3.626 Å. The Rb^+ ion lies on a centre of inversion, and is coordinated by the six oxygens of the crown

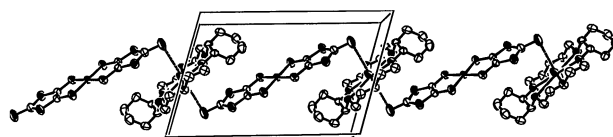


Fig. 4 Crystal structure of $[\text{Rb}(\text{anti-dchyl-18c6})][\text{Ni}(\text{dmit})_2]$ **2** viewed normal to the (010) plane.

ether at distances of 2.804, 2.739 and 2.945 Å. A plane defined through the three inequivalent oxygen atoms and the Rb^+ shows an average deviation for these atoms of 0.099 Å. As the Rb^+ ion lies on the centre of inversion, however, it is clearly positioned exactly within the plane defined by the six coordinating oxygens. No structures containing Rb^+ complexed by dicyclohexyl-8-crown-6 have previously been reported¹⁰ and around 10 have been reported using the parent 18-crown-6 ligand. In almost all of these examples the Rb^+ adopts a position outside of the plane of the oxygens in the crown, either sandwiched between two crowns¹¹ or stabilised by interaction with a counter ion.¹² Such geometry is not surprising when considering the ionic radius of Rb^+ of 1.48 Å in comparison with the estimated cavity size of the crown of 1.34–1.43 Å.¹³ In addition to salt **2** reported here, however, other related $[\text{Ni}(\text{dmit})_2]^-$ salts have recently been discovered which also fully contain the Rb^+ within the plane of the crown, namely $[\text{Rb}(\text{diamino-18-crown-6})][\text{Ni}(\text{dmit})_2]$ ^{14,15} and $[\text{Rb}(\text{18-crown-6})][\text{Ni}(\text{dmit})_2]$.¹⁶

The structure obtained by single crystal analysis was shown by powder X-ray diffraction to be the same phase as the bulk material obtained by mixing Rb^+ , *anti*-dchyl-18c6 and $[\text{Ni}(\text{dmit})_2]^-$ in acetonitrile and leaving to stand overnight. Variable-temperature magnetic susceptibility measurements were carried out on the powder sample. The magnetic behaviour could be fit by the Curie–Weiss expression with one $g = 2$ unpaired electron per nickel complex as expected for the paramagnetic monoanionic species. A value of $\theta = -3.6$ K for the Weiss constant indicated little interaction between adjacent spins which reflects the relatively weak interactions between adjacent complexes mediated by the interaction of terminal sulfur atoms through the Rb^+ ion. This contrasts with the salts $[\text{M}(\text{diamino-18-crown-6})][\text{Ni}(\text{dmit})_2]$ ($\text{M} = \text{K}$ or Rb)¹⁶ where monoanionic metal complexes linked through $\text{S} \cdots \text{M} \cdots \text{S}$ contacts behaved as a one-D Heisenberg antiferromagnetic chain with $J/k_B = 24.7$ and 22.7 K respectively. In these cases the contacting sulfurs were those directly coordinated to Ni and this is presumably the origin of the larger magnetic coupling.

[Cs(anti-dchyl-18c6)]₂[Ni(dmit)₂] 3. This crystallised in the space group $P2_1/c$ and again consists of a sandwich-like arrangement of crown ether-complexed Cs^+ ions around a central metal complex with a centre of inversion on the Ni atom. In contrast to the related Rb^+ structure **1** however the Cs^+ ion is much more centrally positioned above the nickel complex and shows the shortest contact with the nickel itself of 3.472 Å (Fig. 5). The $\text{Ni} \cdots \text{S}$ distances are therefore more similar than in the related Rb-containing structure at 2.194(2) and 2.1838(15) Å. A comparison of the $\text{Ni} \cdots \text{S}$ distances indicates these to be typically shorter than those reported for other dianionic $[\text{Ni}(\text{dmit})_2]^{2-}$ salts (e.g. mean Ni–S bond length in $[\text{NBu}_4]_2[\text{Ni}(\text{dmit})_2]$ is 2.216(6) Å¹⁷). Thus the axial Cs^+ ions appear to result in a closing-in of the sulfur atoms towards the nickel and hence towards the Cs^+ which illustrates the attractive interaction between these components. The interactions of the Cs^+ with the four metal-coordinated sulfur atoms range from 3.733 to 4.440 Å. The Cs^+ is coordinated by the six oxygen atoms of the crown ether at distances from 2.994 to 3.286 Å and lies 1.2906 Å out of a plane formed by the oxygen atoms towards the $[\text{Ni}(\text{dmit})_2]^{2-}$ counter ion. This Cs^+ is out of the crown ring by more than the Rb^+ in the analogous salt **1** and this is typical of related 18-crown-6 structures due to the larger

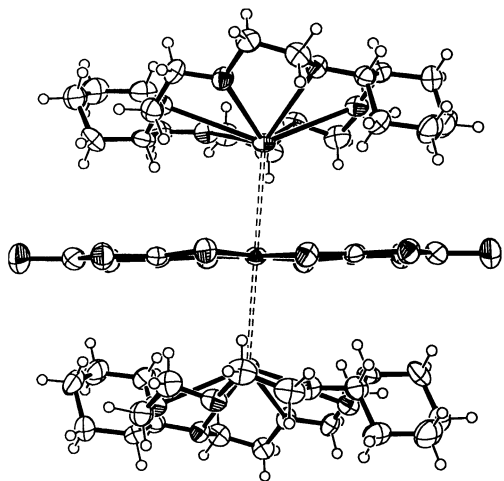


Fig. 5 Crystal structure of $[\text{Cs}(\text{anti-dchyl-18c6})]_2[\text{Ni}(\text{dmit})_2]$ **3** viewed along the short axis of $[\text{Ni}(\text{dmit})_2]^{2-}$.

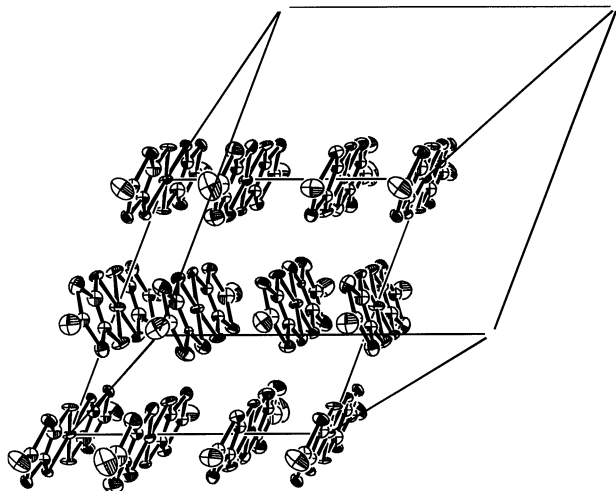


Fig. 6 Crystal structure of $[\text{Cs}(\text{anti-dchyl-18c6})_{1.5}][\text{Ni}(\text{dmit})_2]_6$ **4** showing stacking of the metal complexes. Disordered counter ions are removed for clarity.

ionic radius of Cs^+ . The oxygens show an average deviation from this plane of 0.1554 Å and form an angle with the planar $[\text{Ni}(\text{dmit})_2]^{2-}$ unit of 12.84° . No structures have previously been reported containing Cs^+ coordinated by dicyclohexyl-18-crown-6¹⁰ although around 30 have been reported using the parent crown compound 18-crown-6. Similar to the Rb^+ analogues, these typically show Cs^+ coordinated outwith the ring and stabilised by a second crown or by interaction with the counter ion. Again, such behaviour is expected by a comparison of the Cs^+ ionic radius of 1.69 Å with the estimated crown cavity size of 1.34–1.43 Å.¹³

$[\text{Cs}(\text{anti-dchyl-18c6})_{1.5}][\text{Ni}(\text{dmit})_2]_6$ **4.** This crystallises in the space group $P\bar{1}$ and shows a 2-D sheet of stacked metal complexes with a herringbone-type packing motif. This consists of two crystallographically independent stacks (Fig. 6), each containing two crystallographically independent nickel centres. All of the nickel complexes are essentially planar with average deviations from the plane of 0.0124, 0.0329, 0.0380 and 0.0428 Å. Each stack has an ABAABA repeat pattern with the B Ni located on a centre of inversion. This leads to two different interplanar separations and overlaps within each stack. For both stacks, overlap between $\text{A} \cdots \text{A}$ shows a more slipped arrangement than that between $\text{A} \cdots \text{B}$. This effectively results in trimerisation of the metal complexes within each stack and this non-uniform stacking is presumably the origin of the

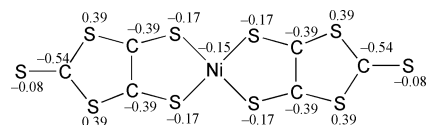


Fig. 7 Partial charges on $[\text{Ni}(\text{dmit})_2]^{2-}$ in salt **1** or **3** as determined by DFT calculations.

semiconducting behaviour of the salt with a room temperature conductivity of $10^{-2} \text{ S cm}^{-1}$ and band gap of 0.2 eV.

The sheets are separated by the crown-complexed Cs^+ counter ions in a ratio of one Cs^+ per six nickel complexes with disorder in the region of the crown-complexed Cs^+ . No other $[\text{Ni}(\text{dmit})_2]^{x-}$ salt has previously shown a ratio of cation to anion of 1 : 6 with the previously highest ratio of 1 : 4 shown in $[\text{AsPh}_4][\text{Ni}(\text{dmit})_2]_4$ ¹⁸ and $[\text{Na}(\text{anti-dchyl-18c6})][\text{Ni}(\text{dmit})_2]_4 \cdot 2\text{C}_3\text{H}_6\text{O}$.⁹ It has been noted that control of the salt stoichiometry can be achieved *via* variation in the size of the counter ion and it appears that the $[\text{Cs}(\text{anti-dchyl-18c6})_{1.5}]^+$ unit is large enough to stabilise the uniquely high ratio. Owing to the considerable disorder in the crystals (see Experimental section) confirmation of the salt stoichiometry was sought by other experimental methods. Density measurement was carried out on the single crystals by flotation in hexane–bromoform and was determined to be 1.859 g ml^{-1} . This compares favourably with the calculated value of 1.839 g ml^{-1} considering that a change in caesium composition would have a relatively large effect on density. Caesium analysis was carried out on the bulk, microcrystalline material by atomic absorption spectroscopy and gave a figure of $2.05 \pm 0.05\%$ Cs by weight, which is close to the theoretical figure of 2.23%. Magnetic susceptibility measurements, carried out on the microcrystalline sample, however were not consistent with the anticipated number of unpaired electrons and could not be fit by the Curie–Weiss expression with meaningful values for the constants. Taken together, these results suggest that the crystals within the sample correspond to the 1 : 6 ratio formula given but that the bulk sample may contain other minor impurities that contribute to the magnetic measurement.

Calculations

Owing to the unique structures displayed by salts **1** and **3**, calculations were carried out more fully to understand the electronic nature of the complexes and the interaction between the crown-complexed Cs^+/Rb^+ ion and the nickel complex. Thus, a series of *ab initio* calculations were performed using the density functional formalism. Previous calculations on $[\text{Ni}(\text{dmit})_2]^{x-}$ containing materials have largely been restricted to EHMO calculations on conducting materials to understand the band structure and dimensionality of such salts. Therefore, in addition to illustrating the nature of salts **1** and **3**, DFT calculations will provide an interesting comparison of the nature of the frontier orbitals to the results obtained with the EHMO method.

For both salts **1** and **3** partial charges were calculated which corresponded to a full 1+ charge on the $\text{M}(\text{crown})$ component and a full 2− charge on the nickel complex and are approximately identical for both systems. The 2− charge on the complex is delocalised over the whole species, however significant negative charge is focussed around the central four sulfurs and the nickel (Fig. 7). This presumably provides the origin of the attraction between the positive M^+ fragment and the nickel complex leading to the exceptionally short $\text{Ni} \cdots \text{Cs}$ and $\text{Ni} \cdots \text{Rb}$ interactions. It is not possible to say however to what extent this charge distribution on the complex is controlled by the presence of the M^+ units as the complex is anticipated to be readily polarisable. Consideration of the total charge density of the sandwich unit shows the electron density around the Cs^+ or Rb^+ to be essentially spherical and this is in keeping with a purely electrostatic interaction between the Cs^+ or Rb^+ and the

nickel complex. In contrast, some degree of covalency can be seen between the donor sulfur atoms and the central nickel with the presence of small lobes of electron density on the sulfurs pointing towards the nickel. Clearly, covalent bonding must contribute to this interaction as all the partial charges in that region are negative and electrostatics alone cannot hold the complex together.

The calculated frontier orbitals of salt **3** illustrate the delocalisation over the system with contributions from all atoms of the complex and again results for **1** and **3** are broadly similar. The qualitative form of these orbitals can be compared with that of corresponding orbitals typically obtained in previous calculations using the EHMO method² and is seen to be similar even though the EHMO results are normally obtained from conducting crystals where the charge on the $[\text{Ni}(\text{dmit})_2]$ complex is between 0 and 1– and where intermolecular interactions are with other $[\text{Ni}(\text{dmit})_2]^{x-}$ units in a stacked manner rather than with the electropositive alkali metal ions used here.

Conclusion

We have prepared four salts containing $[\text{Ni}(\text{dmit})_2]^{x-}$ complexes and *cis-anti-cis*-dicyclohexyl-18-crown-6 complexed alkali metal counter ions. All of these show structures not previously observed within the $[\text{Ni}(\text{dmit})_2]^{x-}$ series of salts and this can presumably be attributed to the large size and structural demands of the crown ether molecules in comparison with smaller counter ions more typically studied. The unique sandwich-type arrangement of **1** and **3** leading to short $\text{Ni} \cdots \text{Cs}$ and $\text{Ni} \cdots \text{Rb}$ interactions has been shown with the aid of DFT calculations to be essentially an electrostatic interaction between the M^+ and the dianionic nickel complex with much negative partial charge residing on the central Ni and four coordinated S atoms. The crystallisation of these by electrochemical reduction contrasts with typical electrochemical oxidation methods used to prepare conducting salts based on $[\text{Ni}(\text{dmit})_2]$ whereby oxidation of the $[\text{Ni}(\text{dmit})_2]^-$ precursor is expected. The conducting salt prepared in this work, **4**, shows the highest ratio of anion : cation in any of the conducting $[\text{Ni}(\text{dmit})_2]$ salts and this can be attributed to the size of the crown-complexed counter ion although further analysis was hampered by disorder. Salt **2** is unusual in displaying a structure influenced by intermolecular interactions involving the terminal sulfur atoms on the complex with the metal counter ions to form a linear-chain packing motif.

Experimental

a.c. electrical conductivity measurements were performed using the four-probe method, magnetic susceptibility measurements on a Quantum Design SQUID magnetometer and powder XRD measurements on a Phillips X'PERT PW3020 system.

$[\text{NBu}_4][\text{Ni}(\text{dmit})_2]$ was prepared according to literature methods.¹⁹ Dicyclohexyl-18-crown-6 was purchased from Aldrich and the *cis* and *trans* isomers separated as described previously.⁹

Preparation of salts 1–4

$[\text{NBu}_4][\text{Ni}(\text{dmit})_2]$ (20 mg) in acetone (8 ml) was placed in the anode compartment of an H-shaped cell. *anti*-dchyl-18c6 (100 mg) and MClO_4 ($\text{M} = \text{Rb}^+$ or Cs^+) (50 mg) were placed in the cathode compartment separated by a porous glass frit. A constant current of 1 μA was passed. Crystals of salts **1** and **3** formed in the cathode compartment and of **4** formed in the anode compartment. Crystals of **2** were collected from the anode compartment. Salt **2** was also prepared by mixing filtered solutions of RbClO_4 (34 mg) and *anti*-dchyl-18c6 (70 mg) in 15 ml CH_3CN and $[\text{NMe}_4][\text{Ni}(\text{dmit})_2]$ (102 mg) in 15 ml

CH_3CN . After standing overnight 42 mg of crystals of **2** had formed.

Attempts to obtain CHN analyses for these salts were largely unsuccessful possibly due to difficulties in combustion of such sulfur and metal rich systems compounded by the difficulty in obtaining large quantities of small single crystals. Interpretation of results however has been carried out based on analysis of the single crystals obtained in structural or conductivity studies. Where a bulk sample has been used, for example for magnetic measurements of **2**, the phase and homogeneity of the material was demonstrated by powder X-ray diffraction.

X-Ray crystallography

Datasets for salts **1** and **3** were collected on a Rigaku AFC6R diffractometer at room temperature, for **2** and **4** on a Stoe stadi-4 diffractometer equipped with an Oxford cryosystems LT device operating at 220 K. The structures were solved by direct methods (SIR 92)²⁰ or Patterson methods (DIRDIF).²¹ Compound **4** crystallised as thin plates, and it was necessary to use the program DIRAX to index the diffraction pattern. This implies that the sample studied was not truly single (probably stacks of plates), and this, combined with the generally weak diffraction and extensive disorder, severely compromised the quality of the dataset for **4**. It is important to recognise that it established the connectivity and packing motifs in the Ni–dmit moieties and the caesium occupancy, but very little else.

[Rb(*anti*-dchyl-18c6)]₂[Ni(dmit)₂] 1. $\text{C}_{46}\text{H}_{72}\text{NiO}_{12}\text{Rb}_2\text{S}_{10}$, $\lambda = 0.71070$ Å, space group $P2_1/c$, $a = 14.636(7)$, $b = 8.484(6)$, $c = 24.440(7)$ Å, $\beta = 94.71(3)^\circ$, $V = 3024.5(28)$ Å³, $Z = 2$, $\mu = 2.318$ mm^{−1}, 6966 independent data collected. The structure was refined on F^2 to give $R1 = 0.0455$ ($F > 4\sigma F$), $wR2$ (all data) = 0.1590.

[Rb(*anti*-dchyl-18c6)][Ni(dmit)₂] 2. $\text{C}_{26}\text{H}_{36}\text{NiO}_6\text{RbS}_{10}$, $\lambda = 1.54184$ Å, space group $P2_1/n$, $a = 10.706(3)$, $b = 10.846(3)$, $c = 16.196(4)$ Å, $\beta = 106.999(17)^\circ$, $V = 1798.4(7)$ Å³, $Z = 2$, $\mu = 8.168$ mm^{−1}, 3245 data collected of which 3234 were independent. An absorption correction was performed by Gaussian integration following refinement of the crystal dimensions against a set of 4 scans. The structure was solved using Patterson methods (DIRDIF)²⁰ and refined on F^2 with H atoms in riding model to give $R1 = 0.0449$ ($F > 4\sigma F$), $wR2$ (all data, F^2) = 0.1333.

[Cs(*anti*-dchyl-18c6)]₂[Ni(dmit)₂] 3. $\text{C}_{46}\text{H}_{72}\text{Cs}_2\text{NiO}_{12}\text{S}_{10}$, $\lambda = 0.71073$ Å, space group $P2_1/c$, $a = 14.628(2)$, $b = 8.3769(9)$, $c = 24.692(3)$ Å, $\beta = 93.631(11)^\circ$, $V = 3019.6(6)$ Å³, $Z = 2$, $\mu = 1.908$ mm^{−1}, 5324 independent data collected. The structure was refined on F^2 to give $R1 = 0.0415$ ($I > 2\sigma I$), $wR2$ (all data) = 0.0854.

[Cs(*anti*-dchyl-18c6)]_{1.5}[Ni(dmit)₂]₆ 4. $\text{C}_{66}\text{H}_{54}\text{CsNi}_6\text{O}_9\text{S}_{60}$, $\lambda = 0.71073$ Å, space group $P\bar{1}$, $a = 11.633(6)$, $b = 12.150$, $c = 23.778$ Å, $a = 80.07(3)$, $\beta = 80.11(3)$, $\gamma = 69.10(3)^\circ$, $V = 3070(3)$ Å³, $Z = 1$, $\mu = 2.261$ mm^{−1}, 7619 data collected of which 5749 were independent. The structure was solved using direct methods and refined on F^2 with H atoms in riding model to give $R1 = 0.1186$ ($F > 4\sigma F$), $wR2 = 0.4340$ (all data). Data were corrected for absorption by Gaussian integration. Part-weight $[(\text{crown})\text{Cs}]^+$ cations lie disordered about two crystallographic inversion centres. The occupancies of the two crystallographically independent caesium sites refined to 0.25, and were thereafter fixed at this value. Chemically unreasonable $\text{Cs} \cdots \text{crown}$ contacts within different disorder fragments and high displacement parameters for the crown suggest that these too are part weight, and the occupancies of these were fixed at 0.75. This gives the overall formulation for **4** as $[\text{Cs}(\text{anti-dchyl-18c6})_{1.5}][\text{Ni}(\text{dmit})_2]_6$ which is supported by the experimental

density and caesium analysis. The crown ethers were refined subject to explicit distance and angle restraints. Only the Ni, S and Cs atoms were refined with anisotropic displacement parameters.

CCDC reference numbers 158412–158415.

See <http://www.rsc.org/suppdata/dt/b0/b008299f/> for crystallographic data in CIF or other electronic format.

Calculations

Ab initio calculations were carried out using the CASTEP code.²² Calculations were performed within the density functional formalism using a plane wave basis set and the generalised gradient approximation²³ to treat the many-body effects of electron exchange and correlation. We have chosen this method for a number of reasons; a large enough plane wave basis set is guaranteed to be both converged and complete. This is necessary in calculating properties of such complex materials where many different bonding configurations are possible, since *a priori* knowledge of the likely electronic configuration is not available in this case which would be useful in the choice of a localised atomic/molecular orbital basis set. Also, since the basis set is complete, we can make use of the Hellmann–Feynman theorem to calculate forces on the atoms for use in geometric optimisation. Vanderbilt ultrasoft pseudopotentials²⁴ are used to describe the valence electron–ionic core interactions which is necessary to reduce the size of the basis set. The electronic wavefunction is expanded in a plane-wave basis set up to a kinetic energy of 500 eV which we find converges the total energy of the system to better than 1 meV per atom. This required the use of approximately 1.8×10^7 basis functions. Brillouin zone integrations were performed by using a Monkhorst–Pack²⁵ *k*-point set. In each calculation presented here a *k*-point density was chosen so that the total energy of the system is also better than 1 meV per atom. The electronic structure was optimised by use of a conjugate gradients energy minimisation scheme. The positions of the atoms within the unit cell were optimised also using a conjugate gradients method and the *ab initio* Hellmann–Feynman forces.

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