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Preparation, structure and properties of [Na(*cis-anti-cis*-dicyclohexyl-18-crown-6)][Ni(dmit)$_2$]$_4$·2Me$_2$CO

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The salt [Na(*cis-anti-cis*-dicyclohexyl-18-crown-6)][Ni(dmit)$_2$]$_4$·2Me$_2$CO (dmit = 1,3-dithiol-2-thione-4,5-dithiolate) has been prepared by electrocrystallisation and characterised by X-ray crystallography showing an unusual 1 : 4 cation : anion ratio. It consists of parallel stacks of [Ni(dmit)$_2$]$^{0.25-}$ complexes separated by the Na$^+$ counter ion complexed by dicyclohexyl-18-crown-6 and two acetone molecules. The electrical conductivity, magnetic susceptibility and thermoelectric power of the salt have been measured and are consistent with semiconductor behaviour which is considered in conjunction with transfer integral calculations.

Introduction

Salts of the complex [Ni(dmit)$_2$]$^{x-}$ have been widely studied due to the high electrical conductivity and, in some cases, superconductivity displayed by these materials.[1] Variation of the counter ion in such salts is known to play a crucial role in determining the intermolecular interactions and packing of the Ni species and hence the conducting properties of the salt. In more recent studies, it has become apparent that counter ions can be introduced which, in addition to playing a structural role in the material, can also introduce additional functionality or unusual properties into the salt. In this context, recent work has included the use of crown-ether complexed counter ions in conducting salts[2] and has led to the isolation of [Li$_{0.6}$(15-crown-5)][Ni(dmit)$_2$]$_2$·H$_2$O, a metallic salt with ion-conducting channels[3] and salts where ion mobility appears to influence conducting behaviour.[4] Such materials provide model systems for mixed electronic–ionic conductors which are important component materials of many battery systems and electrochromics. The study of mixed conductors based on molecular precursors can provide structurally characterised, crystalline materials which offer the opportunity to gain understanding of the structure–property relationships inherent in such materials. The use of crown-ether complexed counter ions also allows the extension of [Ni(dmit)$_2$]$^{x-}$ materials studied to include a wider range of counter ions of differing shapes and geometries and the possibility of new stoichiometries and topologies not previously obtained. Previous studies in this area have been limited to unsubstituted crown ethers and in the light of the unusual structural and materials properties which have arisen we have extended this approach to include substituted crowns. Thus, in the study of such materials using the crown ether *cis-anti-cis*-dicyclohexyl-18-crown-6 (*anti*-dchc), we have isolated the first example of a [Ni(dmit)$_2$]$^{x-}$ salt with this crown (Fig. 1) which shows an unusual 1 : 4 stoichiometry, attributable to the large supramolecular counterion.

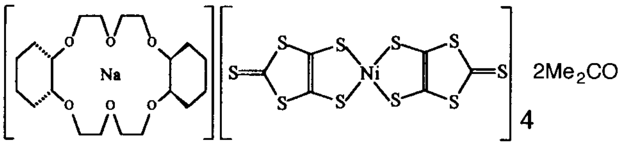

Fig. 1 [Na(*cis-anti-cis*-dicyclohexyl-18-crown-6)][Ni(dmit)$_2$]$_4$·2Me$_2$CO.

Results and discussion

The title salt was prepared by electrocrystallisation of an acetone solution of [NBu$^n{}_4$][Ni(dmit)$_2$] containing *anti*-dchc and NaClO$_4$. The material crystallised in the space group $P\bar{1}$ and the unit cell consists of four [Ni(dmit)$_2$]$^{x-}$ units and one [Na(*anti*-dchc)(Me$_2$CO)$_2$]$^+$ counter ion (Fig. 2). There are two inequivalent [Ni(dmit)$_2$]$^{x-}$ positions giving stacks of the metal complexes along the *c*-axis with an AB repeat pattern (Fig. 3). There are two intrastack interactions. Those within the unit cell have an interplanar distance of 3.559 Å between the A and B complexes which are slipped along the short molecular axis with respect to each other. Those between unit

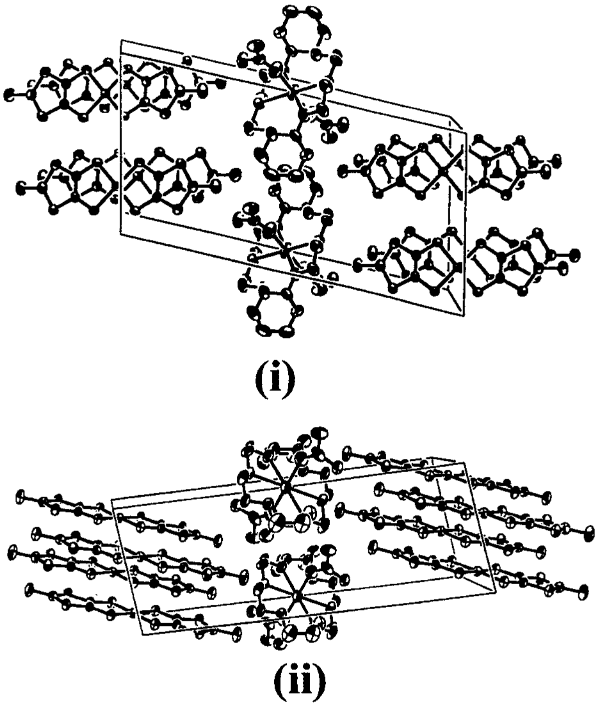

Fig. 2 Unit cell of [Na(*cis-anti-cis*-dicyclohexyl-18-crown-6)]-[Ni(dmit)$_2$]$_4$·2Me$_2$CO viewed along the *c*-axis (i) and the *a*-axis (ii).

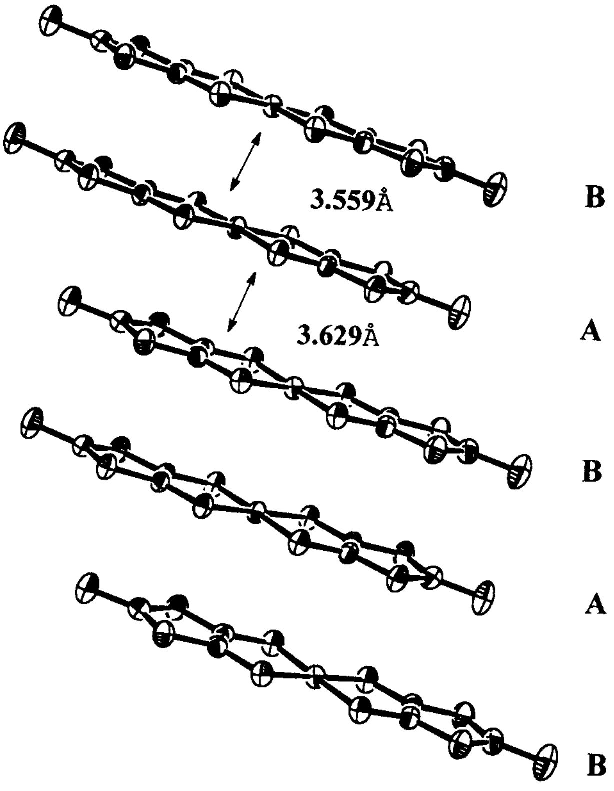

Fig. 3 Stack of $[Ni(dmit)_2]^{0.25-}$ complexes showing interplanar distances.

cells have an interplanar distance of 3.629 Å with an approximate Ni over C arrangement (Fig. 4).

In the counter ion, the Na^+ is positioned at a centre of inversion and is coordinated by four oxygen atoms of the crown ether ring at 2.66 and 2.68 Å with the other two ring oxygens at 2.98 Å. The coordination sphere is increased by the two acetone molecules at a distance of 2.40 Å. Surprisingly, only two salts containing Na^+ complexed by *anti*-dchc have previously been structurally characterised.[5] One of these involves [Co(salen)] [H_2salen = bis(salicylidene)ethylenediamine] units in a more complex arrangement[6] but the structure of the other, [Na(*anti*-dchc)]Br·$2H_2O$,[7] is similar to the structure reported here. This salt also shows Na^+ on an inversion centre with four short (2.67 and 2.68 Å) and two longer (2.967 Å) Na–O bonds and axial OH_2 ligands at 2.35 Å. The absence of any structures involving simple complexation of the Na^+ by the crown without other interactions or solvent inclusion suggests, when considered alongside results obtained here, that such a structural formation is not favoured. As a result, it appears that although *anti*-dchc provides a new structural component for conducting salts it is unlikely to form stacked ion channels in the manner observed in $[Li_{0.6}(15\text{-crown-}5)][Ni(dmit)_2]_2\cdot H_2O$.[3]

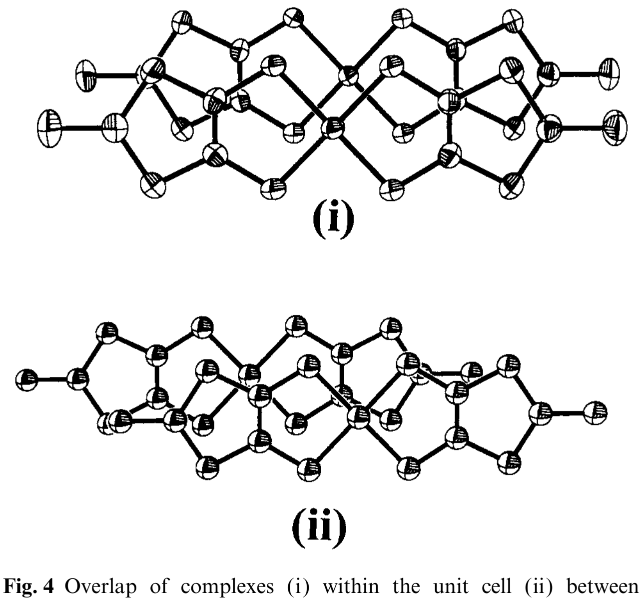

Fig. 4 Overlap of complexes (i) within the unit cell (ii) between adjacent unit cells.

Previous studies of $[Ni(dmit)_2]$-based conducting salts have suggested that the charge on the metal complexes can readily vary to give average fractional charges of *e.g.* 0.5−, 0.29−, 0.25−. An important factor in determining the stoichiometry of the salt appears to be the size of the counter ion and hence the number of $[Ni(dmit)_2]^{x-}$ units required to achieve efficient packing. Previous evidence to support this view can be obtained by a qualitative examination of salts such as $[NMe_4][Ni(dmit)_2]_2$,[8] $[PPh_4][Ni(dmit)_2]_3$,[9] $[NBu_4]_2$-$[Ni(dmit)_2]_7$,[10] and $[AsPh_4][Ni(dmit)_2]_4$[11] where the ratio of cation to anion and hence the average charge per Ni complex is seen to be typically less with the presence of larger counter cations. This pattern is supported by the structure of the title salt as the large supramolecular cation is seen to favour formation of the 1:4 salt. Counter ion size has long been known to control material properties by controlling anion interactions among salts of the same stoichiometry. Results here reinforce the observation that it should also be considered as a straightforward method of controlling the structural composition and average anion charge in the salt and hence influence material properties by this mechanism.

Only one salt, $[AsPh_4][Ni(dmit)_2]_4$, with a $[Ni(dmit)_2]$: cation ratio of 4:1 has been previously structurally characterised.[11] This salt also shows stacks of two crystallographically independent Ni complexes separated by counter ion layers, although a more complex stacking arrangement was observed. The stoichiometry of the title salt indicates an average fractional charge per Ni complex of 0.25−. Comparison of bond lengths within $[Ni(dmit)_2]^{x-}$ molecules have been previously discussed[12] and show that precise information on the fractional oxidation state cannot be obtained by this means. The unusual average charge per Ni complex therefore, does not result in recognisable trends in the bond lengths and angles of the complex, which are similar to those of other fractional oxidation state $[Ni(dmit)_2]$ salts.[12] Also, no assessment can be made of the distribution of charge over the two independent metal complexes, although it seems likely, considering the lack of interaction of the complexes with Na^+, that little charge distribution between the two will occur.

The dc electrical conductivity of crystals of the title salt was measured by the four-probe method over the temperature range 300–220 K and showed semiconductor behaviour with a room temperature conductivity of 0.1 S cm^{-1}. A transition in the activation energy occurs at 250 K with $E_a(<250\ K) = 0.56\ eV$ and $E_a(>250\ K) = 0.13\ eV$ (Fig. 5). Such semiconductor behaviour has been previously observed in $[Ni(dmit)_2]^{x-}$ salts. The application of a hydrostatic pressure resulted initially in an increase in room temperature conductivity by 25% up to 4 kbar. Further increases in pressure resulted in a rapid reduction in conductivity to 5% of the room temperature value by 8 kbar.

The magnetic susceptibility of the salt was measured on a powder sample at a field of 1000 G using a SQUID magnetometer. Measurements above 150 K however, proved unreliable due to the close balance between the paramagnetic and diamagnetic components leading to a susceptibility close to zero and resulting difficulties in signal detection. The large diamagnetic component reflects the unusually large formula unit corresponding to each unpaired spin. The data below 150 K showed Curie–Weiss type behaviour and were fitted to the formula $X = C/(T-\theta) + X_0$ where C, θ and X_0 are the

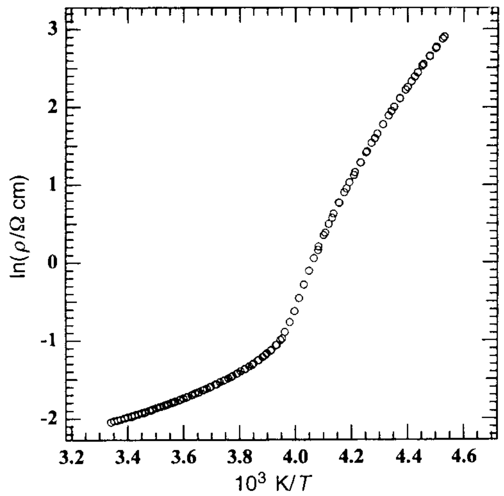

Fig. 5 Log resistivity *vs.* reciprocal temperature from 220 to 300 K.

Curie constant, the Weiss constant and diamagnetic contribution, respectively, with values of $C=0.38$ emu K mol^{-1}, $\theta=-0.44$ and $X_0=114\times10^{-5}$ emu mol^{-1}. The value of C is consistent with one unpaired spin per four nickel complexes with a g value of 2.013. The extremely small Weiss constant of -0.44 K indicates neglible interaction between adjacent localised spins. The magnitude of the diamagnetic contribution from the fit is comparable with that estimated from tabulated values for the component parts of the formula.[13] These measurements give insight into the behaviour of the salt in the low temperature region and are consistent with a localisation of the spins leading to semiconductor behaviour. This suggests that the semiconductor behaviour observed for the material above 220 K continues to be the principal property in the low temperature regime.

The thermoelectric power (S) of the material was measured over the temperature range 210–285 K along the needle axis of the crystal (Fig. 6). Two linear regions can be identified with a transition at 250 K. The transition was shown in this crystal for both the thermoelectric power and the resistance which was simultaneously measured and is in keeping with the transition temperature measured in the conductivity experiment. The region 285–250 K appeared largely temperature independent and the region 250–210 K showed a decrease in S with decreasing temperature. The magnitude of S was negative throughout the temperature range which is indicative of electrons as charge carriers.[14]

It has been shown for systems with strong coulomb interactions[15] that this is the dominant effect[16] in the interpretation of the thermoelectric power which is expected to tend towards a temperature independent value as the temperature is increased, given by[17]

$$S(T\rightarrow\infty)=\left(\frac{-k_\mathrm{B}}{e}\right)\ln\left[\frac{2(1-\rho)}{\rho}\right]$$

where ρ = the number of charge carriers per site. Using the value of $S=102$ μV K^{-1} over the high temperature range 285–250 K a value of $\rho=0.38$ can be calculated.

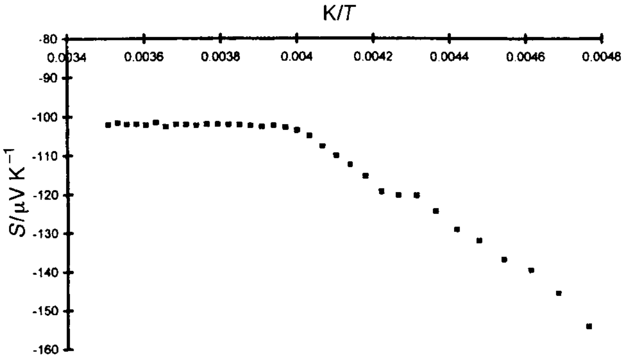

Fig. 6 Thermoelectric power *vs.* reciprocal temperature from 210 to 285 K.

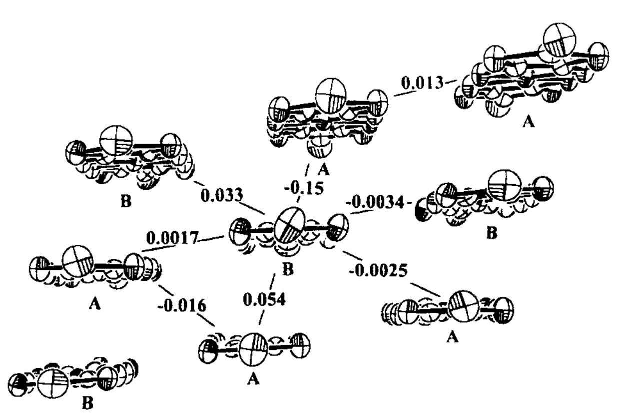

Fig. 7 2-D sheet of stacked complexes showing anions A and B with transfer integrals (eV) calculated by the extended Hückel method.

In considering the lower temperature data (250–210 K), the expression

$$S=-(k_\mathrm{B}/e)(-E_\mathrm{a}/T)+\text{constant}$$

has previously been applied to semiconducting salts.[16] The application of this expression however leads to an activation energy (E_a) of 0.068 eV which is approximately one order of magnitude smaller than the corresponding result from the dc conductivity measurements over this temperature range. This large discrepancy presumably indicates that this expression is not appropriate for this salt and such behaviour has been observed with previous studies of salts where strong coulomb interactions appear to be the dominant effect.

Transfer integrals (t) for the salt were calculated from the overlap integrals (S) using the extended Hückel method and the relation $t=-10$ S eV. Results are shown in Fig. 7. The interactions between [Ni(dmit)$_2$]$^{x-}$ units in the crystal can be described by eight unique transfer integrals. Within the stack there are two interactions and that within the unit cell is shown to be much the larger. Similarly, interstack interactions are dominated by a transfer integral of 0.033 eV between two symmetry equivalent complexes (complex B) within the unit cell. Thus it is anticipated that considerable localisation occurs within the two dimensional sheet of Ni complexes owing to the large differences between interactions within the unit cell and those between cells. Consideration of the thermoelectric power measurement suggests that the conductivity properties can not be readily interpreted by a simple model. The stoichiometry of the salt indicates one unpaired electron per four nickel complexes. For a salt with one electron localised on every fourth site, a value of $\rho=0.25$ would be expected. The measured value of 0.38 presumably arises from the complex arrangement of the structural components and the competing influence of transfer integrals of different magnitudes between pairs of complexes making a simple uniform view of the Ni sites inappropriate. It is also clear that relatively small structural modifications and the resulting influence on transfer integrals would be required to cause the observed transition in activation energy for the salt as the temperature is decreased.

Conclusions

The title salt has been prepared by electrocrystallisation and represents the first [Ni(dmit)$_2$]$^{x-}$ salt with a substituted crown ether complexed counter ion. The material shows an unusually high ratio of $[Ni(dmit)_2]^{x-}$ units to counter ion of 4:1 which can be explained by the incorporation of a large counter ion able to pack efficiently with four $[Ni(dmit)_2]^{x-}$ units. The presence of acetone molecules coordinated to the Na^+ ions prevents any possibility of ion mobility in this salt and suggests that this crown may be a poor candidate for the synthesis of molecular conductors with ion channels and is more suited to the exploration of new crystalline architectures. The salt showed semiconductor behaviour as evidenced by electrical conductivity and magnetic susceptibility measurements. The use of transfer integral calculations indicated that this could be explained by electronic localisation although together with thermoelectric power measurements illustrated the difficulty of applying a simple model owing to a complex structural motif.

Experimental

$[NBu^n{}_4][Ni(dmit)_2]$ was prepared according to literature methods.[18] Dicyclohexyl-18-crown-6 (*cis-syn-cis* and *cis-anti-cis* mixture) was purchased from Aldrich.

Cis-anti-cis-dicyclohexyl-18-crown-6

This is adapted from a literature method[19] using a lower yield procedure more convenient for the isolation of small quantities of the crowns as it avoids the use of H_2S. Dicyclohexyl-18-crown-6 (5.08 g *cis-syn-cis* and *cis-anti-cis* mixture) was stirred in 500 ml deionised water overnight then filtered to remove a small amount of undissolved solid. Perchloric acid (60%, 26 ml) was added dropwise with stirring then after 15 min a second portion was added (9 ml). Stirring was continued for 1 h then the white precipitate of $[H_3O$ (*cis-syn-cis*-dchc]$[ClO_4]$ was filtered off. To the filtrate was added a further portion of perchloric acid (30 ml) and after 90 min a small amount of white solid was filtered off and discarded. The filtrate was extracted with hexane (4 × 150 ml) and the combined extracts washed with water and dried over $MgSO_4$. The volume was reduced to 30 ml and after a few days in a freezer (−20 °C) microcrystalline platelets of the pure *cis-anti-cis* isomer were collected. (Dissolving the $[H_3O$ (*cis-syn-cis*-dchc]$[ClO_4]$ salt in acetone (30 ml) and deionised water (75 ml) followed by a similar extraction procedure yielded the analogous *cis-syn-cis* isomer as large cubes). The separation was confirmed by TLC on silica in methanol–chloroform (1/9) with development of the spots by iodine vapour. The overall combined yield was 51%.

[Na(*anti*-dchc)][Ni(dmit)$_2$]·Me$_2$CO

$[NBu^n{}_4][Ni(dmit)_2]$ (16 mg), *anti*-dchc (100 mg) and $NaClO_4$ (42 mg) were dissolved in dry acetone (15 ml) and placed in the anode compartment of an H-cell. $NaClO_4$ (42 mg) in dry acetone (15 ml) was placed in the cathode compartment separated by a porous glass frit. A constant current of 0.5 μA was passed for 10 days after which needle-like crystals were collected from the anode. Calc for $C_{50}H_{42}O_8S_{40}Ni_4Na$; C, 26.0; H, 1.8; S, 55.4. Found C, 25.8; H, 1.6; S, 57.8%.

Crystal data

All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator at a temperature of 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 55.0°. The structure was solved by heavy-atom Patterson methods and refined with full-matrix least-squares. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 5690 observed reflections $[I > 3\sigma(I)]$. The data were corrected for Lorentz and polarization effects. All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation.

{[Na(*cis-anti-cis*-dchc][Ni(dmit)$_2$]$_4$·2Me$_2$CO: $C_{38}H_{48}O_8S_{20}Ni_2Na$, $M = 1414.38$, space group $\neq P\bar{1}$ (no. 2), $a = 11.452(2)$, $b = 22.823(4)$, $c = 8.509(1)$ Å, $\alpha = 97.44(1)^\circ$, $\beta = 99.32(1)^\circ$, $\gamma = 77.60(1)^\circ$, $V = 2133.2(6)$ Å^3, $Z = 2$, $\mu = 19.33$ cm^{-1}, $D_c = 2.202$ g cm^{-3}, $F(000) = 1454.00$, $R = 0.048$, $R_w = 0.049$, GOF = 3.83.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/148.

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