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Preparation and Structure of $[Na.15\text{-crown-}5][Ni(mnt)_2].H_2O$†

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The salt $[Na.15\text{-crown-}5][Ni(mnt)_2].H_2O$ has been prepared by electrocrystallisation and characterised by X-ray crystallography showing a stacking arrangement of $[Ni(mnt)_2]^-$ and a slipped stack arrangement of the crown ethers.

Metal dithiolene complexes have been widely studied due to their ability to form conducting salts and magnetic materials facilitated by intermolecular contacts between metal complexes.[1,2] Increasingly in recent years, such metal complexes and the analogous tetrathiafulvalene-based organic electron donors have been used as building blocks in more complex supramolecular architectures where control of intermolecular interactions and unusual structural topologies are pursued.[3] This has involved for example, introduction of paramagnetic species as counterions of the conducting stack,[4] or the derivatisation of the redox-active molecules with crown ether groups.[5]

The preparation of dithiolene based molecular conductors containing crown-ether complexed counterions has been reported recently using $[Ni(dmit)_2]^{X-}$ anions. This has led to a series of molecular conductors where the position and possible mobility of counterions is governed by the structural arrangement of crown-ether molecules which, in turn, can influence the behaviour of the conducting electrons in such a system.[6] Thus mixed electronic/ionic conductors have been prepared for molecular precursors. In order to develop an understanding of the structural features of these unusual materials, we have sought to expand this family of salts to include not only other crowns and alkali metal ions but also other metal dithiolenes. During the pursuit of this work we prepared by electrochemical crystallisation and structurally characterised a metal dithiolene salt containing the $[Ni(mnt)_2]^-$ complex with a crown-ether complexed counterion of 1:1 stoichiometry (Fig. 1). This represents the first of such crown-containing dithiolene materials with a metal complex other than $[Ni(dmit)_2]^{X-}$. Salts of this metal complex have shown properties such as high conductivity[7] and unusual magnetic behaviour such as the low temperature ferromagnet, $[NH_4][Ni(mnt)_2].H_2O$.[2]

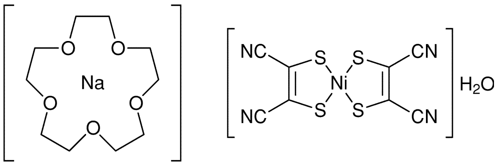

Fig. 1 $[Na.15\text{-crown-}5][Ni(mnt)_2].H_2O$

The title salt was prepared by electrocrystallisation of a solution of $Na_2[Ni(mnt)_2].3H_2O$ (0.2 g), 15-crown-5 (0.24 g) and urea (0.3 g) in water–methanol (30:10, 40 ml) at 1 μA for 27 d. Shiny dark needles of several millimetre length grew at the anode and formed in the anode compartment. (Found C, 35.9; H, 3.6; N, 9.3; S, 21.0. $C_{18}H_{22}O_6N_4S_4NiNa$ requires C, 36.0; H, 3.7; N, 9.4; S, 21.3).

Crystal Data for $C_{18}H_{22}O_6N_4S_4NiNa$.—$M = 600.32$, monoclinic space group $P2_1/c$, $a = 7.307(6)$, $b = 23.104(6)$, $c = 15.949(4)$ Å, $\beta = 99.58(4)°$, $U = 2655(1)$ Å^3, $F_{000} = 1236.00$, $T = 296$ K, $Z = 4$, $D_{calc} = 1.502$ g cm^{-3}, $\lambda(MoK\alpha) = 0.71069$ Å, $\mu(MoK\alpha) = 11.01$ cm^{-1}, $R = 0.065$, $R_w = 0.046$. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Research (S)*, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 423/13.

Preparation of the title material was achieved by electrochemical oxidation of the corresponding dianionic dithiolene salt. It has been previously demonstrated that preparation of monoanionic $[Ni(mnt)_2]^-$ salts by chemical oxidation requires rapid precipitation[7] of the product to avoid disproportionation and contamination of the product with the neutral and dianionic species. The electrochemical method has proven an important alternative suitable for the preparation of single crystals since slow crystal growth from solution occurs as the monoanion is formed and no disproportionation can occur. Previous studies however, for example with $[NH_4][Ni(mnt)_2].H_2O$, have demonstrated that more than one crystallographic phase can be obtained by electrochemical methods which can result in difficult interpretation of solid-state properties.[8] The procedure reported represents a high purity route to large needles of several millimetres length of a $[Ni(mnt)_2]^-$ salt. The title salt differs from related dithiolene-containing materials in both

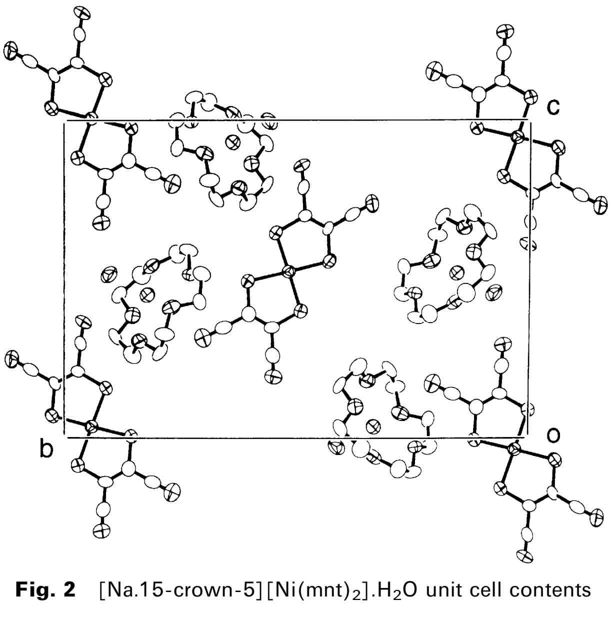

Fig. 2 $[Na.15\text{-crown-}5][Ni(mnt)_2].H_2O$ unit cell contents

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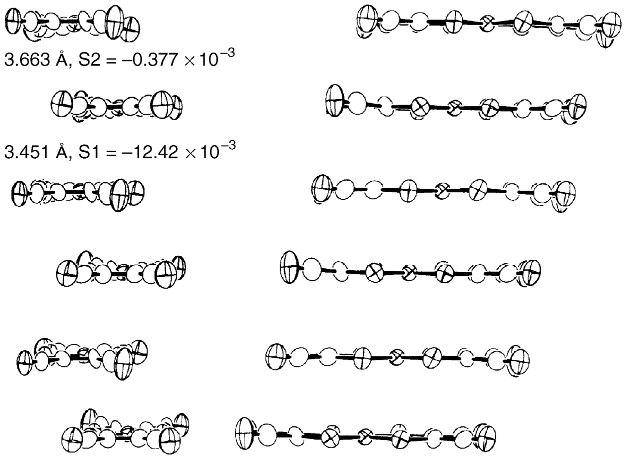

Fig. 3 Stack of $[Ni(mnt)_2]^-$ anions showing intermolecular spacing and transfer integrals

the 1:1 stoichiometry and the incorporation of a dithiolene complex other than $[Ni(dmit)_2]^-$. The previous lack of examples of such crown ether–$[Ni(mnt)_2]^-$ materials reflects the greater difficulty in the preparation of $[Ni(mnt)_2]^-$ salts by electrocrystallisation compared with $[Ni(dmit)_2]^-$ systems due to the reduced capacity for intermolecular contacts and hence, in general, less ease of formation of conducting crystals.

The structure consists of stacks of $[Ni(mnt)_2]^-$ anions with stacks of 15-crown-5 molecules running approximately parallel to these. The $[Ni(mnt)_2]^-$ complexes display geometry consistent with previously reported structures.[9] Fig. 2 shows the arrangement of anions and cations in the unit cell.

The $[Ni(mnt)_2]^-$ anions are slightly dimerised giving rise to two different separations of 3.451 and 3.663 Å between the mean molecular planes of the complexes in the stack (Fig. 3). This structural type is expected for a 1:1 salt but the dimerisation is much less marked than in related structures with larger counterions such as $[N(C_4H_9)_4][Ni(mnt)_2]$ or $[N(C_2H_5)_4][Ni(mnt)_2]$.[9] This also contrasts with salts such as $[NH_4][Ni(mnt)_2].H_2O$ and $K[Pd(mnt)_2]$ where the very small counterions led to a uniform stack of metal complex anions.[10] EHMO calculations were carried out for the stacked $[Ni(mnt)_2]^-$ ions and gave values of $S1 = -2.42 \times 10^{-3}$ and $S2 = -0.377 \times 10^{-3}$ for the overlap integrals within the stacks for the short and long intermolecular contacts respectively (Fig. 3). The strong dimerisation indicated by these values is consistent with magnetic susceptibility measurements which show Bleaney–Bowers type behaviour[11] with $J/k_B = -195$ K and is also consistent with the low room temperature conductivity of 10^{-5} Scm^{-1} displayed by the salt.

The cation stacks show molecules of 15-crown-5 tilted at an angle of 37.3° with respect to the stacking axis (Fig. 4). The Na^+ ions are encapsulated within the oxygen ring and are also coordinated by the oxygen of the water molecule. This stacking arrangement appears to preclude the possibility of ion mobility within the crown ether stacks.

Outwith the area of dithiolene complexes, some related species have been prepared containing the electron acceptor TCNQ (*e.g.* [K.18-crown-6][TCNQ]) where some evidence was presented for metal ion migration and for the modification of electronic properties by inclusion of crown ethers compared with the analogous alkali-metal salts of TCNQ.[12] The salt described in this work may be regarded as intermediate in both composition and properties between the family of highly electronically conducting crown-containing $[Ni(dmit)_2]^{X-}$ salts and the crown-containing TCNQ materials.

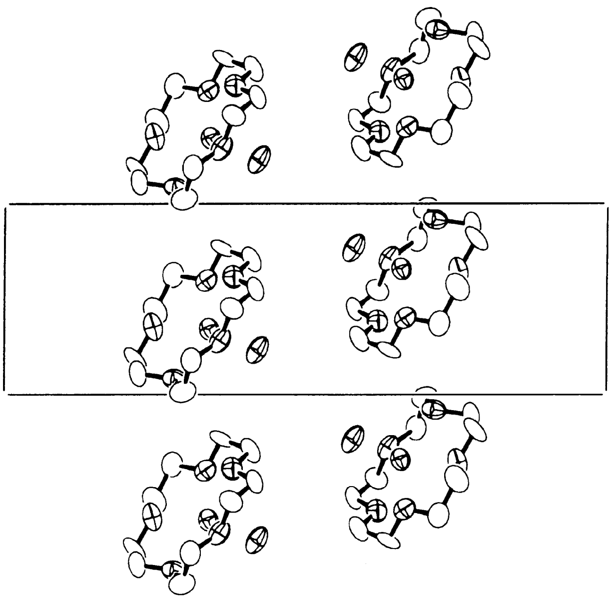

Fig. 4 Slipped stack of $[Na.15\text{-crown-}5].H_2O$ units

In conclusion we have prepared and structurally characterised a metal dithiolene salt containing a supramolecular counterion consisting of Na^+ ions bound in a 15-crown-5 molecule.

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