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Synthesis, structure and properties of [ethylpyridinium][Ni(mnt)$_2$]: evidence for an unusual magnetically ordered ground state

Neil Robertson,[a]* Christoph Bergemann,[b] Helmut Becker,[b] Prabhat Agarwal,[b] Stephen R. Julian,[b] Richard H. Friend,[b] Nicholas J. Hatton,[c] Allan E. Underhill[c] and Akiko Kobayashi[d]

[a]*Department of Chemistry, University of Edinburgh, West Mains Rd., Edinburgh, UK EH9 3JJ*
[b]*Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge, UK CB3 OHE*
[c]*Department of Chemistry, University of Wales, Bangor, Gwynedd, UK LL57 2UW*
[d]*Department of Chemistry, School of Science, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan*

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[Ethylpyridinium][Ni(mnt)$_2$] has been prepared by electrochemical oxidation of the corresponding dianionic salt. The X-ray structure has been determined. Three different environments were observed for the paramagnetic anions with two in a stacking mode and one approximately orthogonal to the stack. The stacking showed an ACA-type repeat unit with an inversion centre on complex C. Magnetic susceptibility measurements show Curie–Weiss behaviour with a change in parameters at around 50 K. Above this temperature a Curie constant of 0.3 emu K mol^{-1} and a Weiss constant of -150 K were observed and below 50 K these values were 0.08 emu K mol^{-1} and $+2$ K respectively. A maximum in the susceptibility was observed at 285 mK which suggests low temperature ordering to a phase with a non-cancelled alignment of the spins. Intermolecular interactions and the effect of temperature were assessed in terms of transfer integral calculations.

Introduction

Metal complexes of 1,2-dithiolenes are known to display cooperative solid-state behaviour which can lead to properties such as metallic conductivity,[1] superconductivity[1,2] and unusual magnetic ground states.[3] In particular, square-planar, paramagnetic metal complexes of the maleonitriledithiolate ligand (mnt^{2-}) have been studied with a variety of central metals and closed-shell counterions[4] and as components of more complex charge-transfer salts with counterions such as viologen,[5] perylene[6] or BEDT-TTF.[7] In general, the series [M(mnt)$_2$]$^-$ (M = Ni, Pd, Pt) with large counterions such as tetraalkylammonium show structures with dimers of $S = 1/2$ metal complexes leading to a diamagnetic ground state and a thermally accessible triplet state.[8] Studies with smaller counterions such as Li$^+$, Na$^+$, K$^+$ however, were undertaken to encourage strong, long-range, cooperative effects allowing the possibility of more varied magnetic and conducting ground states.[9] In this context, studies of the salt [NH$_4$][Ni(mnt)$_2$]·H$_2$O showed a ferromagnetic ground state[10,11] arising from a uniform stack[12] of [Ni(mnt)$_2$]$^-$ units. Furthermore, studies on the salt [BDNT]$_2$[Ni(mnt)$_2$][13] (Fig. 1) revealed a ferromagnetic ground state arising from the contribution of the [Ni(mnt)$_2$]$^-$ component alongside high conductivity (0.5 S cm^{-1}) arising from the organic component which illustrates the potential of such complexes as components of hybrid systems. As such ferromagnetic behaviour is rare,[14] we sought to further explore salts of this anion and to focus on planar counterions as these may encourage a close-stacked interaction of the metal complexes, analogous to the NH$_4$$^+$ salt, which appears to be a key element of the ferromagnetic behaviour. We report studies of the ethylpyridinium (Etpy) salt showing unusual magnetic behaviour and discuss this in terms of a uniquely complex packing motif.

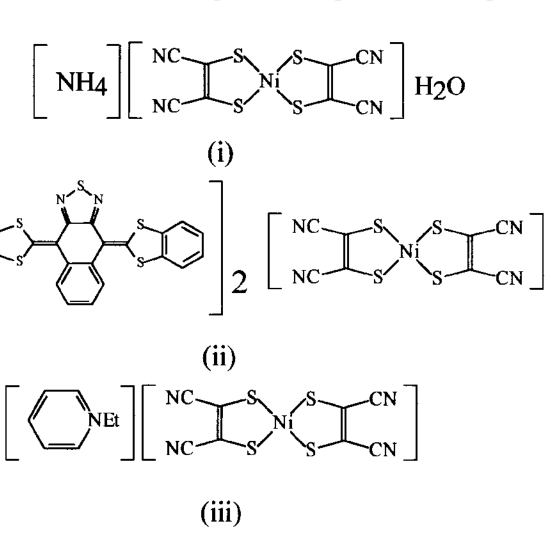
Results and discussion

Preparation

The title salt was prepared by electrochemical oxidation of the salt [Etpy]$_2$[Ni(mnt)$_2$] to deposit the product on the anode, followed by recrystallisation of this powder from CH$_2$Cl$_2$. Although chemical oxidation of the dianion, by I$_2$ for example, can also lead to the monoanionic complex, it has been found that the electrochemical method generally gives rise to a higher purity product more suitable for subsequent solid-state measurements.

X-Ray structure

The structure was determined at 296 K and at 20 K. Both structures showed the same space group ($P\bar{1}$) and the same overall packing motif (Fig. 2) but with differences in interatomic contacts which can significantly modify cooperative properties. Both structures consist of three non-equivalent anions and three non-equivalent cations with some disorder in one of the Etpy cations. Bond lengths in the [Ni(mnt)$_2$]$^-$ complexes are shown in Table 1 and indicate that all the complexes are best formulated as monoanionic and are comparable with literature examples.[12] Comparison of the param-



(i)

(ii)

(iii)

Fig. 1 [NH$_4$][Ni(mnt)$_2$]·H$_2$O (i), [BDNT]$_2$[Ni(mnt)$_2$] (ii), [Etpy][Ni(mnt)$_2$] (iii).

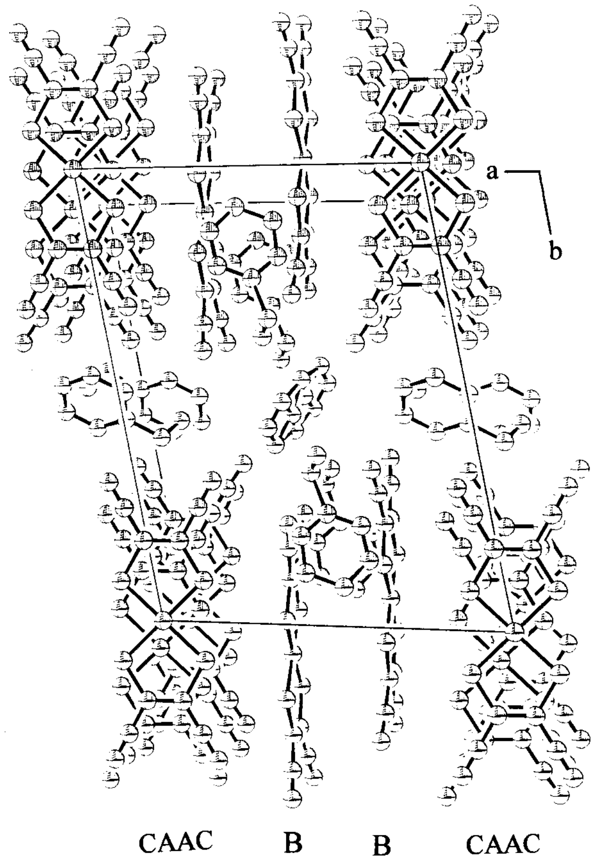


Fig. 2 Structure of [Etpy][Ni(mnt)$_2$] at 296 K viewed along the *c*-axis.

eters at 296 K and 20 K shows that the intramolecular parameters show no consistent variations upon reduction in temperature. All of the nickel complexes can be shown to be highly planar, in particular around the central NiS_4C_4 core, with little deviation from the least squares planes (Table 2, Fig. 3). Deviations of the atoms of the CN groups from these planes are larger but also fairly small.

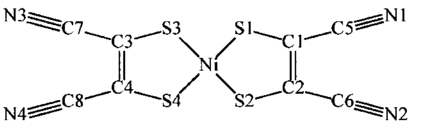


Fig. 3 Atom numbering scheme for Table 1.

Table 1 Bond lengths for [Ni(mnt)$_2$]$^-$ complexes at 296 K and 20 K (Fig. 4)

	296 K			20 K		
	A	B	C	A	B	C
Ni–S1	2.152(2)	2.147(3)	2.148(3)	2.160(1)	2.152(1)	2.146(1)
Ni–S2	2.148(3)	2.139(3)	2.153(2)	2.151(1)	2.145(1)	2.158(1)
Ni–S3	2.159(3)	2.145(3)	—	2.152(1)	2.147(1)	—
Ni–S4	2.146(2)	2.138(3)	—	2.155(1)	2.141(1)	—
S1–C1	1.71(1)	1.71(1)	1.725(9)	1.716(4)	1.727(4)	1.717(3)
S2–C2	1.723(9)	1.750(9)	1.75(1)	1.719(3)	1.730(3)	1.705(4)
S3–C3	1.715(9)	1.694(9)	—	1.721(3)	1.706(3)	—
S4–C4	1.722(9)	1.69(1)	—	1.703(4)	1.718(4)	—
N1–C5	1.15(1)	1.15(2)	1.15(2)	1.150(4)	1.144(5)	1.156(5)
N2–C6	1.16(2)	1.14(2)	1.17(2)	1.154(5)	1.156(5)	1.149(5)
N3–C7	1.14(2)	1.16(2)	—	1.152(5)	1.166(5)	—
N4–C8	1.19(1)	1.16(1)	—	1.158(4)	1.147(4)	—
C1–C2	1.35(1)	1.35(1)	1.32(1)	1.383(5)	1.334(6)	1.384(5)
C3–C4	1.36(1)	1.40(1)	—	1.378(5)	1.360(6)	—
C1–C5	1.44(1)	1.42(1)	1.41(2)	1.441(4)	1.441(5)	1.427(5)
C2–C6	1.41(1)	1.40(2)	1.43(1)	1.430(5)	1.444(5)	1.441(5)
C3–C7	1.44(1)	1.40(2)	—	1.432(5)	1.414(5)	—
C4–C8	1.37(1)	1.41(1)	—	1.433(5)	1.446(4)	—

Two of the Ni species are stacked along the *c*-axis with an ACA-type repeat unit and a centre of inversion on the C-nickel. This gives rise to two different overlaps characterised by different short S···S contacts between the stacked molecules (Fig. 3, Fig. 4, Table 3). Both overlaps are based on a nickel-over-sulfur arrangement but with the AC overlap more slipped from this geometry than the AA′ overlap.

Lying approximately orthogonal to the stack is the other non-equivalent metal complex (B) and this displays short S···S and S···Ni contacts to the stacking complexes and to another molecule of B linking to the next stack (Fig. 4). Although there are short contacts between complex B and the stack, the almost orthogonal arrangement suggests that overlap between these will be negligible. This is evidenced by the dihedral angles of the complexes B and the stacking complexes (Table 2). This structural motif is unprecedented in the chemistry of [M(mnt)$_2$]$^-$ complexes and an examination[15] of related salts with planar aromatic counterions shows all of the [Ni(mnt)$_2$]$^-$ arranged in segregated or mixed stacks.[6,16] The only similar structure of which we are aware is that of [PPh$_4$][Ni(dmit)$_2$]$_3$ which also shows stacks containing two of the metal complexes with a third positioned adjacent and orthogonal.[17] In stoichiometry and materials properties however, this salt shows no other relationship.

The influence of temperature is displayed in the structure determination at 20 K where all the intermolecular S···S and S···Ni contacts are observed to be significantly shorter than in the corresponding room temperature structure (Fig. 4, Table 3). This results in reduction of the cell volume from 2346.6(5) Å^3 to 2239.8(8) Å^3 at the lower temperature. Such variations in intermolecular contacts can lead to large changes in the materials properties of the salt due to the subtle interplay between ferromagnetic and antiferromagnetic components of the intermolecular interactions. Calculations have suggested that when the intermolecular distance in stacked [Ni(mnt)$_2$]$^-$ units is reduced, the change in dominant Ni···Ni to Ni···S interactions can result in a change from antiferromagnetic to ferromagnetic behaviour.[10] Thus we may anticipate that variable temperature magnetic studies of such systems can include behaviour associated with gradual changes in intermolecular interactions as well as changes in population of electronic levels with temperature. Such effects will be more marked for species such as the title salt, with non-covalent linking of magnetic centres, rather than for covalent or ionic lattices.

Magnetic measurements

Magnetic susceptibility measurements were carried out directly on the microcrystalline product prepared by electrocrystallisation and on the material recrystallised from dichloromethane. Both samples showed identical behaviour and measurements carried out on samples from different preparations consistently showed the same properties.

The magnetic susceptibility of polycrystalline [Etpy][Ni(mnt)$_2$] was measured from 100 mK to room temperature. The magnetic behaviour shows a transition around 50–60 K (Fig. 5). Above this temperature, the salt exhibits Curie–Weiss behaviour with a Curie constant of 0.3 emu K mol^{-1} and a Weiss temperature of -150 K which indicates strong antiferromagnetic coupling. A Curie constant of around 0.375 emu K mol^{-1} would be expected for one $g=2$ unpaired spin per molecule.

Below 50 K, the Curie–Weiss behaviour changes character, and the salt now displays a positive Weiss temperature of around 2 K and a Curie constant of 0.08 emu K mol^{-1}, corresponding to just 22% of the value of one $g=2$ unpaired spin per molecule. Towards lower temperatures, the inverse susceptibility trace is very slightly rounded, shifting the Weiss

Table 2 Deviations from, and dihedral angles between, least squares planes defined by Ni,S1,S2,S3,S4,C1,C2,C3,C4 (Fig. 3)

	296 K			20 K		
	A	B	C	A	B	C
Mean deviation of Ni,S1,S2,S3,S4,C1,C2,C3,C4/Å	−0.020	0.039	0.000	−0.020	−0.030	0.000
Mean deviation of C5,C6,C7,C8,N1,N2,N3,N4/Å	−0.075	−0.205	0.022	−0.095	−0.215	0.033
	A–C	B–C	A–B	A–C	B–C	A–B
dihedral angles/°	3.81	89.20	92.14	3.91	88.07	91.33

Table 3 Intermolecular transfer integrals (×1000), interplanar distances and short intermolecular contacts (Fig. 3)

Interaction (Fig. 4)		296 K	20 K
AA′	1000*t*/eV	0.428	0.365
	Interplanar/Å	3.565	3.479
	Ni···Ni/Å	3.963	3.885
	Ni···S4/Å	3.715	3.657
AC	1000*t*/eV	0.565	0.927
	Interplanar/Å	3.648	3.509
	Ni···Ni/Å	4.050	4.039
	Ni(C)···S4(A)/Å	3.699	3.570
	Ni(A)···S2(C)/Å	3.668	3.526
BB	1000*t*/eV	1.25	2.01
	Interplanar/Å	3.522	3.381
	Ni···S4/Å	3.685	3.587

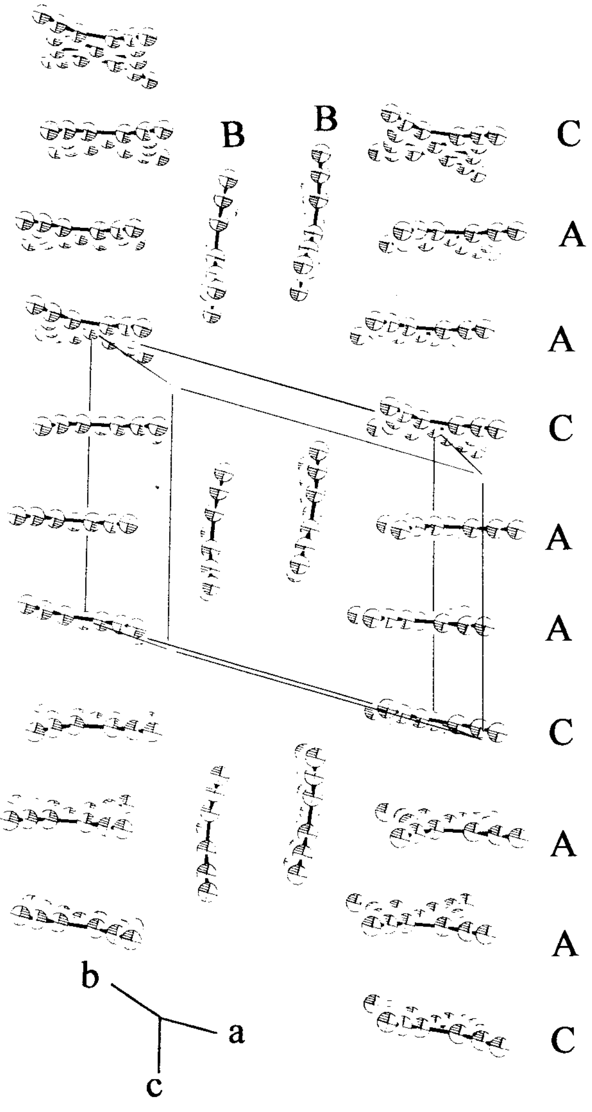


Fig. 4 Stacking of $[Ni(mnt)_2]^-$ at 296 K with $[Etpy]^+$ removed for clarity.

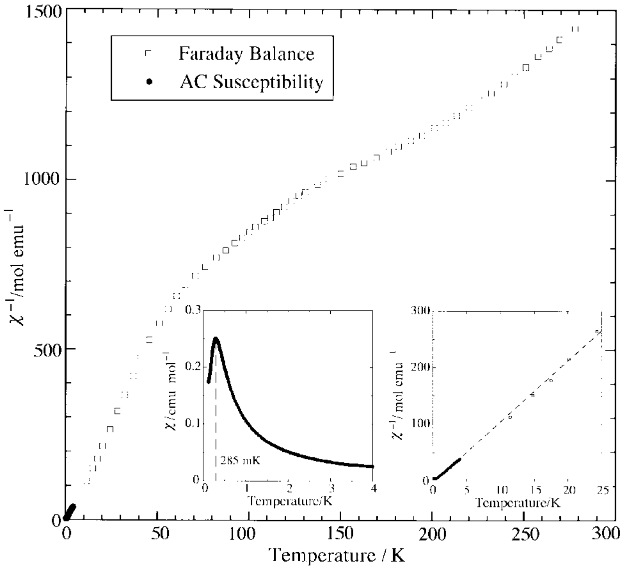


Fig. 5 Magnetic susceptibility of $[Etpy][Ni(mnt)_2]$ showing Faraday balance and AC susceptibility results.

temperature marginally lower and raising the Curie constant to 0.094 emu K mol^{-1}. At 285 mK, the susceptibility shows a pronounced maximum, suggesting a transition into a low-temperature ordered magnetic state with a non-cancelled spin configuration. Attempts to detect non-linear effects such as hysteresis or saturation near the suspected transition, through analysis of the in-phase signal and the third harmonic at the lock-in amplifier respectively, remained unsuccessful. This may be due to the low excitation fields (0.066 mT up to 0.66 mT) used in the study as higher drive currents heated the sample beyond the transition temperature. Finally, very preliminary torque magnetometry results on a single crystal in the temperature range 1.5 K to 25 K indicate a noticeable anisotropy of the magnetic response at low temperatures.

The electrical conductivity of a compressed pellet of the salt was measured at room temperature by the four-probe method and showed a value of 10^{-5} S cm^{-1} which is consistent with related salts[4] and as expected for a material with a non-uniform stacking arrangement and a 1 : 1 ratio of cations to anions.

Discussion

We interpret these observations of the variable temperature magnetic behaviour as an indication of some uncompensated spin ordering arising from incomplete antiferromagnetic cancellation of the unpaired electrons. Such behaviour normally arises from a spin canting mechanism whereby neighbouring spins are aligned in an antiferromagnetic manner but not exactly antiparallel, and has been previously observed in low dimensional molecular systems composed of sulfur–nitrogen radicals[18] or nitroxide radicals.[19] The mechanism for spin canting[20] requires that the spins in the solid are not related by a centre of inversion. Inspection of the structure of

[Etpy][Ni(mnt)$_2$] reveals that although a centre of inversion is present, within the stacks it relates only those spins on complexes A and B. Complex C is located on the inversion centre and therefore has no symmetry equivalent in the stack.

Spin canting may arise through a Dzyaloshinsky–Moriya interaction, the magnitude of which is proportional to $\Delta g/g$. Although the g-parameters for the complexes would be expected to be modified by interactions in the solid state, the likely magnitude of the anisotropy can be illustrated by consideration of the g-parameters of [Ni(mnt)$_2$]$^-$ in a CH_2Cl_2 frozen glass. These can be determined as 2.01, 2.05 and 2.15, which shows considerably greater anisotropy than in the radical p-NCC_6F_4CNSSN[18] where a spin canting mechanism is believed to operate.

Additionally, the title salt shows an unusually complex structural motif composed of three independent spin-1/2 anionic complexes (Fig. 1). Despite this unique structure, the complex [Etpy][Ni(mnt)$_2$] shows remarkably similar properties in magnetic behaviour to the other [Ni(mnt)$_2$]$^-$ salts where ferromagnetic exchange was observed, namely [NH_4][Ni(mnt)$_2$]$\cdot H_2O$[10,11] and [BDNT][Ni(mnt)$_2$].[13] All three salts show a negative Weiss constant at high temperatures and a change in behaviour to a positive Weiss constant as the temperature is reduced. This is accompanied by a change in Curie constant to a lower value.

For the ammonium salt, this transition was interpreted on the basis of McConnell's spin polarisation model and overlap of the stacked [Ni(mnt)$_2$]$^-$ complexes whereby a change from antiferromagnetic to ferromagnetic behaviour was proposed to occur as the intermolecular stacking distance was reduced. For the BDNT salt however, no structural data were available. In the case of the title salt, the complex structural motif leads to a variety of different intermolecular interactions and it is unlikely that a simple explanation for the spin ordering can be expected. The uncompensated spin alignment may arise from one of the sublattices only or from a complex interplay of interactions between them.

The ammonium salt displayed hysteresis with a coercive field of 100 Oe and a hard and easy magnetisation axis. In contrast, for the BDNT salt and the title salt no hysteresis effects were measured. In these cases however, no oriented single crystal measurements were available due to a lack of structural data in the former case and the difficult experimental conditions at 285 mK in the latter.

Transfer integrals (t/eV) have been calculated between the interacting neighbours from the structure of the title salt at both 296 K and 20 K using the extended Hückel method and are shown in Table 3. The low value shown by all these interactions is in keeping with the presumably weak interactions between neighbours leading to the extremely low temperature of magnetic ordering. The reduction in temperature appears to result in a stronger interaction between the A and C complexes which would lead to the effective division of the structure into weakly interacting ACA units and BB dimers. This is in contrast to the more typical structures of [Ni(mnt)$_2$]$^-$ salts with large anions where simple dimers lead to spin cancellation and a diamagnetic ground state. This again points to the role of the unusual structure of the title salt in the observed magnetic behaviour. In addition, although the magnitude of the transfer integrals is small, the relative variations of these with temperature are large which emphasises the influence that a change in temperature can play in the magnetic properties of a molecular solid.

Conclusions

The salt [Eypy][Ni(mnt)$_2$] has been prepared by electrocrystallisation and structurally characterised at 296 K and 20 K showing a unique arrangement of the metal complexes on three non-equivalent sites. Magnetic susceptibility measurements have indicated a magnetic transition at 285 mK which appears to arise from incomplete cancellation of spins and this has been discussed in terms of the symmetry and complex packing adopted by the salt. Transfer integral calculations have served to illustrate the nature of the packing arrangement and to demonstrate the large variations in intermolecular interactions which can take place upon varying temperature.

Experimental

High temperature susceptometry was performed using a Faraday balance on a continuous flow ^{4}He cryostat, in an accessible temperature range from 10 K to room temperature. A Cahn 2000 electrobalance sensed the magnetic force on a polycrystalline sample in a field gradient of 15 T m^{-1}, at a field of 0.95 T.

Low temperature AC susceptibility measurements were carried out on an adiabatic demagnetisation cryostat, capable of reaching 100 mK in one-shot mode. Data were taken during the slow warm-up, typically at about 10 mK h^{-1}. A copper drive coil, operated at 0.5 mA (RMS) at 77 Hz, generated an excitation field of about 1 mK above base temperature. The magnetic signal of the [Etpy][Ni(mnt)$_2$] sample (mass 2.5 μg) was detected using a compensated pair of copper pick-up coils, preamplified, and fed into an EG&G lock-in amplifier. While a precise absolute first-principles calibration of the set-up was not possible, a rough estimate of the expected pick-up voltages per susceptibility yielded susceptibility values compatible with the previous Faraday balance data but had to be scaled up by about 15% to match those data exactly. Above 3.5 K, helium bath level effects and superconducting transitions of the solder junctions obscured the signal.

[Etpy]$_2$[Ni(mnt)$_2$]

This was prepared by analogy to literature methods for tetraalkylammonium salts.[21]

[Etpy][Ni(mnt)$_2$]

[Etpy]$_2$[Ni(mnt)$_2$] (0.175 g, 0.31 mmol) and urea (0.30 g) were stirred in a degassed mixture of H_2O (40 ml) and acetone (10 ml) and then filtered to remove a small amount of undissolved solid. A constant current of 3 μA was passed through the solution for four weeks using a platinum plate anode. A dark microcrystalline solid was scraped from the anode and washed with H_2O to yield 28 mg of product (0.063 mmol, 20% yield). Calc. for $C_{15}H_{10}N_5S_4Ni$, C, 40.3; H, 2.2; N, 15.7; S, 28.6. Found C, 40.5; H, 2.3; N, 16.2; S, 26.7%.

Crystal data for [Etpy][Ni(mnt)$_2$] at 296 K

$NiN_5C_{15}S_4H_{10}$, $M = 447.22$, triclinic, $P\bar{1}$, $a = 13.311(2)$, $b = 17.093(1)$, $c = 11.016(1)$ Å, $\alpha = 95.095(8)$, $\beta = 105.20(1)$, $\gamma = 101.189(10)°$, $V = 2346.6(6)$ Å^3, $\mu = 11.89$ cm^{-1}, $Z = 4$, calc. density = 1.266 g cm^{-3}. Data were collected on an automatic four-circle diffractometer (Rigaku AFC5R) using Mo(Kα) radiation ($\lambda = 0.71069$ Å). A total of 10779 unique reflections were collected to a maximum 2θ of 55.0° and 5034 reflections with $I > 3.0\sigma(I)$ were used in the structural analysis. The structure solution was obtained by direct methods using SIR92 and all calculations performed using the teXsan crystallographic software package.[22] Hydrogen atoms were included but not refined. The structure converged to $R1 = 0.087$ and $Rw = 0.161$.

Crystal data for [Etpy][Ni(mnt)$_2$] at 20 K

$NiN_5C_{15}S_4H_{10}$, $M = 447.22$, triclinic, $P\bar{1}$, $a = 13.055(3)$, $b = 16.915(3)$, $c = 10.772(2)$ Å, $\alpha = 95.66(1)$, $\beta = 105.00(1)$, $\gamma = 99.65(1)°$, $V = 2239.8$ Å^3, $\mu = 12.46$ cm^{-1}, $Z = 4$, calc. density = 1.326 g cm^{-3}. Data were collected by the Weissenberg type low-temperature IP system (MAC SCIENCE DIP-320) with a helium refrigerator using Mo(Kα) radiation ($\lambda = 0.71069$ Å). A total of 9294 reflections were collected to a maximum 2θ of 61.1° and 6759 reflections with $I > 4.0\sigma(I)$ were used in the structural analysis. All calculations were performed by the teXsan crystallographic software package.[22] Hydrogen atoms were included but not refined. The structure converged satisfactorily to $R1 = 0.068$ and $Rw = 0.107$.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See 'Information for Authors', *J. Mater. Chem.*, Issue 1, available *via* the RSC web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/161.

See http://www.rsc.org/suppdata/jm/1999/1713/ for crystallographic files in .cif format.

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