A unique new multiband molecular conductor: [BDTA][Ni(dmit)$_2$]$_2$†

Sarah S. Staniland,[a] Wataru Fujita,[b] Yoshikatsu Umezono,[b] Kunio Awaga,[b] Stewart J. Clark,[c] HengBo Cui,[d] Hayao Kobayashi[d] and Neil Robertson*[a]

A new molecular conducting material, [BDTA][Ni(dmit)$_2$]$_2$, with a novel multiband electronic structure has been prepared by simple mixing of precursor salts of the components.

Metal *bis*-1,2-dithiolene-based materials yield novel properties such as superconductivity,[1] non-linear optical[2] and magnetic interactions[3] and in particular, [M(dmit)$_2$]$^{x-}$ salts (dmit = 1,3-dithiol-2-thione-4,5-dithiolate, M = Ni, Pd) have yielded numerous conducting and superconducting materials. These involve both simple counterions *e.g.* [N(CH$_3$)$_4$][Ni(dmit)$_2$]$_2$ and also open shell cations *e.g.* [TTF][Ni(dmit)$_2$]$_2$ (TTF = 1,4,5,8-tetrathiafulvalene).[4a] Such open-shell cations can lead to a multi-band system, where the material retains enhanced stability towards structural distortion and charge-localisation, however well-characterised [M(dmit)$_2$]$^{x-}$ salts with such non-innocent, open-shell counterions are rare. These are largely limited to the TTF^{x+} family of cations where partial charge-transfer can result and more recently to salts with verdazyl radicals.[4b] Planar, sulfur-rich, dithiazolyl cations have formed many novel materials with interesting magnetic properties due to strong intermolecular interactions,[5] and include the magnetic material with the highest ordering temperature of any organic magnet.[6] In this report, the cation [BDTA]$^+$ (BDTA = benzo-1,3,2-dithiazolyl), has been crystallised with [Ni(dmit)$_2$]$^{x-}$ by simple mixing of precursor salts to give a novel multiband conducting system (Fig. 1).

Single crystals of [BDTA][Ni(dmit)$_2$]$_2$ were prepared by a diffusion method through slow mixing of solutions of [BDTA][Cl][7] and [NBu$^t_4$][Ni(dmit)$_2$].[8] The 1:2 stoichiometry can be rationalised by considering the redox potentials (against SCE), $E_{1/2}$ = +0.15 V for [BDTA]$^{1+/0}$ and +0.22 V for [Ni(dmit)$_2$]$^{0/1-}$, which evidently are sufficiently similar to allow redox reaction to accompany crystallisation of the product. The crystals have the space group $P\bar{1}$ with one [Ni(dmit)$_2$] and half of one BDTA cation per asymmetric unit, with an inversion centre along C7–C8 of BDTA creating an intrinsic disorder between the 5- and 6-membered rings of the cation.‡ The [Ni(dmit)$_2$]$^{x-}$ units stack along the [110] direction (Fig. 2) with alternate interplanar distances of 3.468 and 3.563 Å, similar to the structure of [N(CH$_3$)$_4$][Ni(dmit)$_2$]$_2$.[9] Short contacts
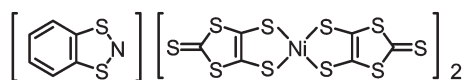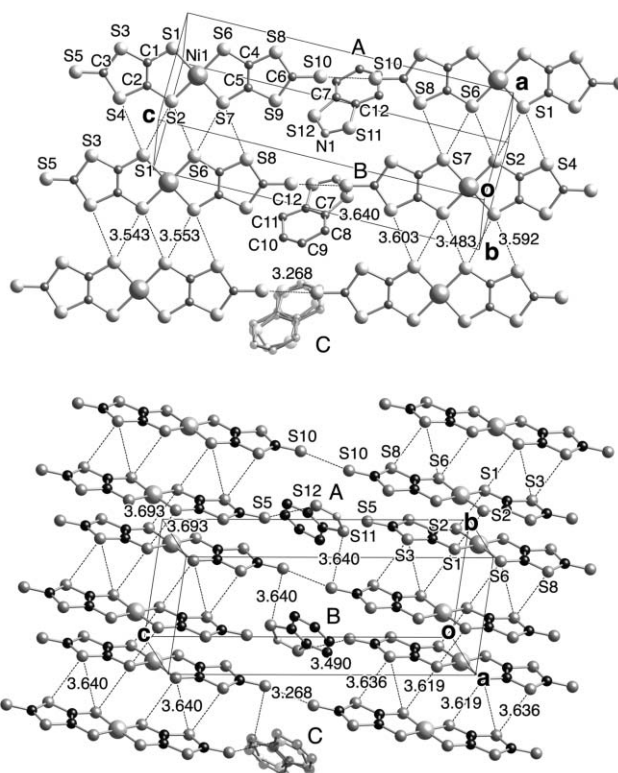

Fig. 1 [BDTA][Ni(dmit)$_2$]$_2$.

Fig. 2 X-ray structure of [BDTA][Ni(dmit)$_2$]$_2$ showing short S···S contacts. BDTA is disordered and the two orientations are shown (A and B) along with the disordered molecule C.

are seen between [Ni(dmit)$_2$]$^{x-}$ complexes on adjacent stacks, both side-by-side between S1–S2, S1–S4, S6–S2, S6–S7 and S7–S8 and diagonally between S3–S8, S3–S6 and S6–S1, as well as to the adjacent sheet through the terminal S10 (Fig. 2). Short contacts are also seen between the terminal sulfur atoms and the BDTA cation, although due to disorder, only half of these contacts will exist in any unit cell.

[BDTA][Ni(dmit)$_2$]$_2$ shows room-temperature conductivity of 0.1 S cm^{-1} and semiconductor behaviour over the range 80–200 K with a small activation energy of 0.19 eV.† The band structure was calculated using plane-wave DFT methods and shows significant dispersion in the stacking and the side-by-side directions (Fig. 3) which is comparable with other conducting [Ni(dmit)$_2$] systems.[10] The HOMO of the cation [BDTA]$^{x+}$ and the LUMO of the anion [Ni(dmit)$_2$]$^{0.5x-}$ form the frontier orbitals at the Fermi level† and the very narrow band gap arises due to an avoided crossing of these bands. The calculated charges on each atom were summed and gave the anion an overall charge of −0.12 and the [BDTA]$^{x+}$
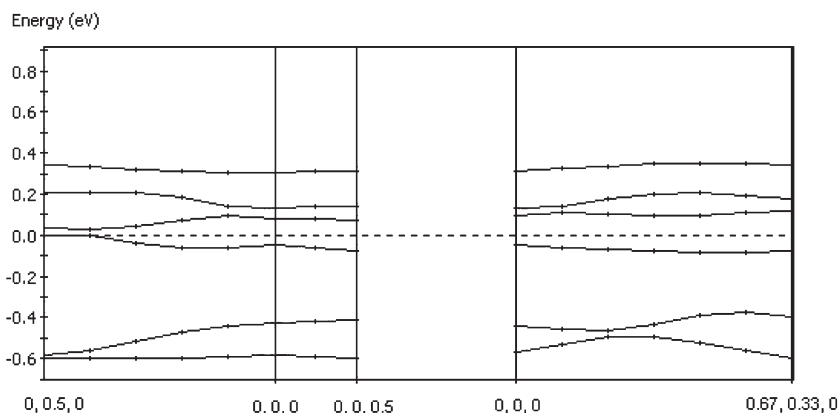
Fig. 3 Band structure calculated using DFT plane wave methods showing bands around the Fermi level (dotted line).

cation a charge of +0.24. In order to perform the band calculation, the disordered $[BDTA]^{x+}$ species was fixed into a single orientation, however the key conclusions involving the energy of the BDTA band and the form of $[Ni(dmit)_2]^{x-}$ based bands can still be inferred from the results.

$[BDTA][Ni(dmit)_2]_2$ must have (at least) one unpaired electron per formula unit and the molar magnetic susceptibility shows a peak around 25 K with a further increase in susceptibility at lower temperatures.† Fitting the data requires the use of a combination of two models involving both isolated Curie spins and coupled spins, which we represented using a 1D AF Heisenberg S = ½ chain model. This gave a Curie constant corresponding to 73%, and a fit to the chain model corresponding to 27% of the value expected for one unpaired electron, consistent with the fractional charges shown in the DFT calculation. The magnetic coupling between electrons in the chain is $J/k_b = -55$ K, presumably arising due to the intermolecular interaction between the $[Ni(dmit)_2]^{x-}$ ions shown in the band structure calculation.

In conclusion, $[BDTA][Ni(dmit)_2]_2$ has been prepared by simple mixing of precursor salts. The synthesis, X-ray structure, magnetic susceptibility data, band structure and conductivity data are all consistent with a charge-transfer system, involving a fractional average charge on both the anion and the cation leading to a multi-band conducting material. We believe this to be the first well-characterised example of a salt containing partially-oxidised $[BDTA]^{x+}$ as well as a new type of open-shell counterion for $[Ni(dmit)_2]^{x-}$. We thank the EPSRC and The University of Edinburgh for financial support.

Sarah S. Staniland,[a] **Wataru Fujita,**[b] **Yoshikatsu Umezono,**[b] **Kunio Awaga,**[b] **Stewart J. Clark,**[c] **HengBo Cui,**[d] **Hayao Kobayashi**[d] **and Neil Robertson**[*a]
[a]*School of Chemistry, University of Edinburgh, King's Building's, Edinburgh, UK. E-mail: neil.robertson@ed.ac.uk; Fax: +44 131 6504743; Tel: +44 131 6504755*
[b]*Department of Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan. E-mail: awaga@mbox.chem.nagoya-u.ac.jp; Fax: +81 52 7892484; Tel: +81 52 7892487*
[c]*Department of Physics, University of Durham, South Road, Durham, UK*
[d]*Institute for Molecular Science and CREST, JST, Okazaki, Japan*

Notes and references

‡ Single crystals of $[BDTA][Ni(dmit)_2]_2$ were prepared by slow diffusion of [BDTA]Cl in MeCN with $[NBu^t_4][Ni(mnt)_2]$ in dichloromethane. Small,

green, hexagonal plate shaped crystals were collected after 12 days. More rapid mixing gave a microcrystalline bulk sample which was washed with MeCN and ether ($C_{18}H_4NNi_2S_{22}$. Calculated; C, 20.45; H, 0.38; N, 1.33. Found; C, 20.45; H, 0.27; N, 1.38%). The bulk sample was shown by powder X-ray diffraction to be the same phase as the single crystal used in the structure determination, and was then used for the magnetic and conductivity measurements.

X-ray Crystallography data: X-ray diffraction intensities were collected on a new Rigaku X-ray diffractometer equipped with confocal X-ray mirror system and a CCD detector with Mo–K-α radiation at room temperature. $C_9H_2NiN_{0.5}S_{11}$, M = 530.49, Triclinic, a = 6.454(4), b = 7.448(4), c = 19.603(10) Å, α = 99.707(5), β = 91.077(5), γ = 115.569(6)° U = 833.5(8) Å^3, T =293.1 K, space group $P\bar{1}$, Z = 2, μ(Mo–Kα) = 2.529 mm^{-1}, 4560 reflections were collected, 1803 independent reflections with R_{int} = 0.0690 were used in all calculations. The final $wR(F^2)$ ($I > 3\sigma I$) was 0.032. An empirical absorption correction was carried out after data reduction. The structure was solved by direct methods and refined by full-matrix least squares against F^2 using all data (SHELXTL). H-atoms were not included due to the disorder of the BDTA component. All non-H atoms were modelled with anisotropic displacement parameters. CCDC 265314. See http://www.rsc.org/suppdata/cc/b5/b502783g/ for crystallographic data in CIF or other electronic format.

DFT plane wave calculations were performed using the density functional formalism within the generalized gradient approximation using the CASTEP code.[11] The electronic wavefunctions are expanded in a plane wave basis set up to a kinetic energy cut off of 380 eV which converges the total energy of the system to better than 1 meV per atom. The valence electron and ion interactions are described using ultrasoft pseudo potentials. Integrations over the Brillouin zone are performed on a grid which also converges the total energy of the system to 1 meV per atom. Geometry optimizations are performed by relaxing the positions and unit cell parameters under the influence of the Hellmann–Feynman forces and stresses respectively.

1 P. Cassoux, *Coord. Chem. Rev.*, 1999, **185–186**, 213.
2 P. Romaniello and F. Lelj, *Chem. Phys. Lett.*, 2003, **372**, 51.
3 N. Robertson and L. Cronin, *Coord. Chem. Rev.*, 2002, **227**, 93.
4 (*a*) M. Bousseau, L. Valade, M. F. Bruniquel, P. Cassoux, M. Garbauskas, L. Interrante and J. Kasper, *Nouveau Journal de Chimie*, 1984, **8**, 3; L. Brossard, M. Ribault, L. Valade and P. Cassoux, *Physica B + C (Amsterdam)*, 1986, **143**, 378; A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita and W. Sasaki, *Chem. Lett.*, 1987, 1819; A. Kobayashi, H. Kim, Y. Sasaki, S. Moriyama, Y. Nishio, K. Kajita, W. Sasaki, R. Kato and H. Kobayashi, *Synth. Met.*, 1988, **27**, B339; K. Mukai, T. Hatanaka, N. Senba, T. Nakayashiki, Y. Misaki, K. Tanaka, K. Ueda, T. Sugimoto and N. Azuma, *Inorg. Chem.*, 2002, **41**, 5066; (*b*) K. Mukai, N. Senba, T. Hatanaka, H. Minakuchi, K. Ohara, M. Taniguchi, Y. Misaki, Y. Hosokoshi, K. Inoue and N. Azuma, *Inorg. Chem.*, 2004, **43**, 566.
5 J. M. Rawson and G. D. McManus, *Coord. Chem. Rev.*, 1999, **189**, 135; E. G. Awere, N. Burford, R. C. Haddon, S. Parsons, J. Passmore, J. V. Waszczak and P. S. White, *Inorg. Chem.*, 1990, **29**, 4821; T. M. Barclay, A. W. Cordes, N. A. George, R. C. Haddon,

M. E. Itkis, M. S. Mashuta, R. T. Oakley, G. W. Patenaude, R. W. Reed, J. F. Richardson and H. Zhang, *J. Am. Chem. Soc.*, 1998, **120**, 352; S. S. Staniland, W. Fujita, U. Yoshikatsu, K. Awaga, P. J. Camp, S. J. Clark and N. Robertson, *Inorg. Chem.*, 2005, **44**, 546.

6 A. J. Banister, N. Bricklebank, I. Lavender, J. M. Rawson, C. I. Gregory, B. K. Tanner, W. Clegg, M. R. J. Elsegood and F. Palacio, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2533.

7 G. Wolmershauser, M. Schnauber and T. Wilhelm, *J. Chem. Soc., Chem. Commun.*, 1984, 573.

8 G. Steimecke, R. Kirmse and E. Hoyer, *Z. Chem.*, 1975, **15**, 28; G. Steimecke, H. J. Sieler, R. Kirmse and E. Hoyer, *Phosphorus Sulfur Relat. Elem.*, 1979, **7**, 49.

9 H. Kim, A. Kobayashi, Y. Sasaki, R. Kato and H. Kobayashi, *Chem. Lett.*, 1987, 1799.

10 P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev.*, 1991, **110**, 115; H. Kobayashi, R. Kato, A. Kobayashi and Y. Sasaki, *Chem. Lett.*, 1985, 191.

11 M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne, *J. Phys. Condens. Matter*, 2002, **14**, 2717.