Synthesis, structure and properties of nickel complexes of 4,5-tetrathiafulvalene dithiolates: high conductivity in neutral dithiolate complexes

Nathalie Le Narvor,[a] Neil Robertson,[b] Tania Weyland,[c] Jeremy D. Kilburn,*[a] Allan E. Underhill,*[b] Michael Webster,[a] Niels Svenstrup[d] and Jan Becher[d]

[a] *Department of Chemistry, University of Southampton, Southampton, UK SO17 1BJ*
[b] *Department of Chemistry, University of Wales, Bangor, Gwynedd, UK LL57 2UW*
[c] *Laboratorie de Chimie de Complexes de Metaux Transition et Synthetic Organic, URA CNRS 415, Campus de Beaulieu, 35042 Rennes Cedex, France*
[d] *Department of Chemistry, Odense University, DK-5230, Odense M, Denmark*

Dianionic and neutral nickel complexes of substituted TTF dithiolate ligands have been prepared showing room-temperature conductivity of up to 10^{-1} S cm^{-1} for the neutral complexes; the crystal structure of the neutral complex [Ni($C_{10}H_{10}S_8$)$_2$] is reported.

Recently,[1] we reported the synthesis of mercury complexes **1** (Fig. 1) derived from dithiolene ligands[2,3] which contain structural elements of both the dmit ligand and the TTF moiety.[4] In the mercury complex **1**, tetrahedral coordination about the metal centre restricts the possibility of achieving a closely stacked structure in the solid state. Nonetheless the oxidised neutral complex **2** showed a surprisingly high conductivity for an undoped solid of 10^{-5} S cm^{-1} as a compressed pellet. The extension of this series using metals likely to exhibit square-planar coordination should increase the potential for molecular stacking and ligand orbital overlap, which might give rise to compounds with high electrical conductivity. We report here the preparation of nickel complexes of 4,5-tetrathiafulvalene dithiolates as dianionic salts and as neutral complexes.

The air-sensitive dianionic nickel complexes **3a** and **3b** were prepared by deprotection of bis(cyanoethyl)thio substituted TTFs[3] using NMe_4OH, followed by addition of $NiCl_2 \cdot 6H_2O$, in a procedure identical to that used to prepare the mercury complexes **1**.[1] The dianionic complexes could be oxidised to the corresponding, insoluble neutral complexes by reaction with I_2 in acetonitrile which led directly to an analytically pure sample of **4a**. Electrochemical oxidation of **3b** in acetonitrile gave a microcrystalline coating of analytically pure **4b** on the anode, while stirring a suspension of **3c** in EtOH, in the presence of air, gave **4c** again analytically pure.

Polycrystalline lumps of **4b** were grown by slow diffusion through a glass frit of a solution of iodine in acetonitrile into a solution of **3b** and small flakes were cleaved from these lumps for X-ray examination. The structure consists of discrete centrosymmetric molecules (Fig. 2) with the eight ligand S atoms essentially coplanar (maximum deviation 0.19 Å). The geometry at Ni is square planar and the Ni–S distances [2.160(7), 2.172(5) Å] can be compared *e.g.* with those in a bis(dithiooxalato)nickel anion[5] [2.170 (av) Å]. The C–S and C–C distances are unexceptional. The view of the structure down *b* (Fig. 3) shows clearly how the molecules pack together with the perpendicular spacing between the molecules *ca.* 3.4 Å. Because of the 'slipped' nature of the stacking the Ni···Ni distance is 5.167(1) Å (*a*) and the shortest intermolecular Ni···S distance is 3.593(7) Å. The shortest intermolecular S···S

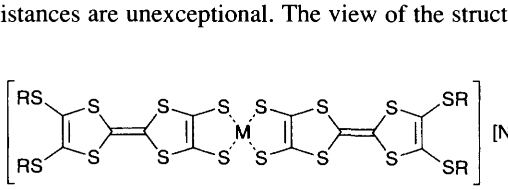

Fig. 1 M = Hg, *n* = 2, R = Et; **2** M = Hg, *n* = 0, R = Et; **3** M = Ni, *n* = 2, R = Bu (**3a**), R = Et (**3b**); **4** M = Ni, *n* = 0, R = Bu (**4a**), R = Et (**4b**), R = Me (**4c**)

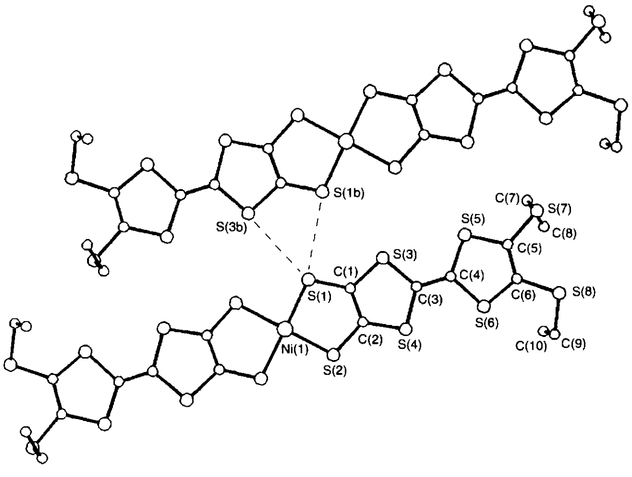

Fig. 2 Two adjacent molecules separated by a unit translation in the *b* direction and viewed perpendicular to the molecules showing the atom labelling and some intermolecular contacts < 3.6 Å. Relevant distances (Å) and angles (°): Ni(1)–S(1) 2.172(5), Ni(1)–S(2) 2.160(7), C(1)–C(2) 1.41(3), C(3)–C(4) 1.39(3), C(5)–C(6) 1.42(3), S–C (ring) 1.68(2)–1.79(3), S–C (non-ring) 1.74(2)–1.88(3), S(1)–Ni(1)–S(2d) 93.3(2), S(1)–Ni(1)–S(2) 86.7(2), Ni(1)–S(1)–C(1) 103.4(7), Ni(1)–S(2)–C(2) 102.1(8), S(1)–C(1)–C(2) 120(2), S(2)–C(2)–C(1) 122(2). Intermolecular contacts: S(1)···S(1b) 3.56(1), S(1)···S(3b) 3.570(8), S(3)···S(3c) 3.51(2). Symmetry operations: b = 1 − *x*, 1 − *y*, 1 − *z*; c = −*x*, 1 − *y*, 1 − *z*.

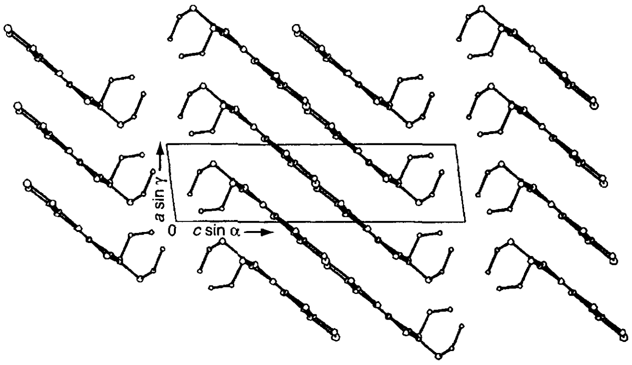

Fig. 3 Packing diagram viewed down the *b* direction

distance is 3.51(2) Å. Fig. 4 shows two molecules related by a translation in the *a* direction when viewed perpendicular to the molecule emphasising the 'slipped' stacking.

Cyclic voltammetry (CV) of complex **3b** was carried out in $\mathrm{CH_2Cl_2}$ using $\mathrm{NBu^n{}_4PF_6}$ as supporting electrolyte at 100 mV $\mathrm{s^{-1}}$ against SCE. When scanned over the potential range -1.0 to $+0.2$ V the CVs showed two oxidations as expected for a nickel dithiolene dianion.[6] The first of these is reversible and occurs at -0.48 V and the second, associated with oxidation to the neutral complex, occurs at -0.07 V with behaviour typical of formation of an insoluble film of the neutral complex on the electrode. The spontaneous aerial oxidation of **3b** to **4b** is consistent with these values. On the reverse scan, two reduction waves were observed at -0.24 and -0.42 V associated with the second oxidation. The CV of **3a** showed qualitatively the same features over similar potential regions.

These results contrast with those displayed by the analogous tetrahedral mercury complexes of these ligands[1] which showed little interaction between the two linked TTF units in the molecule. The nickel complexes described here show a square-planar geometry allowing, for the neutral complexes, pairing of the odd electrons on the two TTF units to occur. Further evidence for this is given by the lack of an ESR signal for the neutral nickel complexes (in the solid state) whereas the neutral mercury complexes gave an ESR spectrum consistent with radicals localised on each ligand. Previous reports of compounds containing linked TTF units have generally described partial or complete localisation of charge on each TTF unit,[8] although recent work by Becker *et al.*[9] reports that for the directly linked TTF dimer (TTF–TTF) the radical cation and dication (formed by two one-electron oxidations) are completely delocalised.

The electrical conductivities of the neutral complexes **4a–c** were measured as compressed pellets by a four-probe method over the range 300–80 K (**4b**, **4c**) and 300–200 K (**4a**) and the results are summarised in Table 1. The conductivity of crystalline **4b**, taken from the same sample as that used for the X-ray analysis, was measured over the range 290–50 K. The room-temperature conductivity (σ_{RT}) was 2.7×10^{-2} S $\mathrm{cm^{-1}}$ and dropped steadily with decreasing temperature indicating semiconducting behaviour. It was not possible however to obtain a linear plot of $\ln(\sigma/\sigma_{\mathrm{RT}})$ against $1/T^n$. The lower conductivity, compared with the compressed pellet, may reflect the anisotropy of the material as the axis of the sample along which conductivity was measured is not necessarily the highest conducting, and also the fact that the crystalline sample of **4b** used was not a true single crystal.

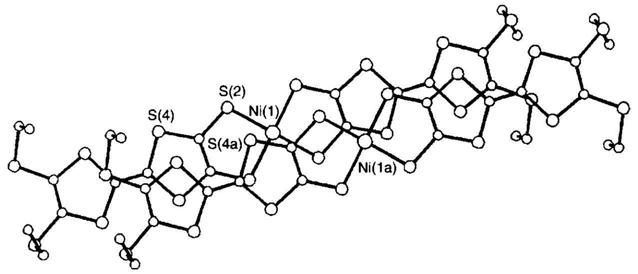

Fig. 4 Two adjacent molecules separated by a unit translation in the *a* direction and viewed perpendicular to the molecules. Intermolecular contact: Ni(1)···S(4a) 3.593(7). Symmetry operation: a = 1 + *x*, *y*, *z*.

Table 1 Conductivity measurements of nickel complexes

Compound	σ_{RT}/S $\mathrm{cm^{-1}}$	
4a	10^{-4}	Semiconductor, BG = 0.23 eV
4b	10^{-1}	Semiconductor, BG = 0.10 eV
4c	10^{-1}	300–275 K, metallic 275–90 K, semiconductor, BG = 0.09 eV

σ_{RT} Values of **4b** and **4c** are significantly higher than values normally observed for neutral complexes of dithiolenes {[Ni(dmit)$_2$] is unusually conductive with $\sigma_{\mathrm{RT}} = 3.5 \times 10^{-3}$ S $\mathrm{cm^{-1}}$, many others have reported values of *ca.* 10^{-6} S $\mathrm{cm^{-1}}$},[10] or for neutral TTF-type systems.[11] As microcrystalline samples of **4b**, **4c** and the crystalline sample of **4b** all show this property it appears unlikely that the high conductivity arises from doping by small amounts of impurities. The high conductivities presumably reflect the improved intermolecular overlap associated with the use of extended ligand π-systems and the large number of sulfur atoms in the ligand framework. The lower conductivity of **4a** shows that the solid-state properties of this class of compound are sensitive to the length of the alkyl chain substituent.

In conclusion we have demonstrated high conductivity in neutral dithiolene complexes of Ni achieved by extending the ligand framework using TTF dithiolates. In addition, the two TTF moieties show significant communication through the metal centre.

We thank the EPSRC for financial support (GR/J26540), for funds to purchase the X-ray diffractometer and C. Lapinte (Rennes) for the use of electrochemical apparatus.

Footnote

† *Crystal Data.* $\mathrm{C_{20}H_{20}NiS_{16}}$, $M = 832.04$, triclinic, space group $P\bar{1}$ (no. 2), $a = 5.167(1)$, $b = 7.787(2)$, $c = 18.867(8)$ Å, $\alpha = 88.04(2)$, $\beta = 97.15(3)$, $\gamma = 95.81(2)°$, $U = 749.1(4)$ Å^3, $F(000) = 424$, $T = 150$ K, $Z = 1$, $D_c = 1.844$ g $\mathrm{cm^{-3}}$, λ(Mo-Kα) = 0.71069 Å, μ(Mo-Kα) = 17.39 $\mathrm{cm^{-1}}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/83.

References

1 N. Le Narvor, N. Robertson, E. Wallace, J. D. Kilburn, A. E. Underhill, P. N. Bartlett and M. Webster, *J. Chem. Soc., Dalton. Trans.*, 1996, 823.

2 C. Gemmell, G. C. Janairo, J. D. Kilburn, H. Ueck and A. E. Underhill, *J. Chem. Soc., Perkin. Trans. 1*, 1994, 2715.

3 J. Becher, J. Lau, P. Leriche. P. Mørk and N. Svenstrup, *J. Chem. Soc., Chem. Commun.*, 1994, 2715.

4 For other reports of TTF derived metal complexes see: N. M. Rivera, E. M. Engler and R. R. Schumaker, *J. Chem. Soc., Chem. Commun.*, 1979, 184; R. D. McCullough, J. A. Belot, A. L. Rheingold and G. P. A. Yap, *J. Am. Chem. Soc.*, 1995, **117**, 9913.

5 P. Roman, J. I. Beitia and A. Luque, *Polyhedron*, 1993, **12**, 2831.

6 D. C. Olson, V. P. Mayweg and G. N. Schrauzer, *J. Am. Chem. Soc.*, 1966, **88**, 4876.

7 R. Greef, R. Peat, L. M. Peter, D. Pletcher and J. Robinson, *Instrumental Methods in Electrochemistry*, Ellis Horwood Ltd, 1990.

8 See for example: C. Wang, A. Ellern, J. Y. Becker and J. Bernstein, *Tetrahedron Lett.*, 1994, **35**, 8489 and references therein; ref. 7 and references therein. See also: M. Adam and K. Müllen, *Adv. Mater.*, 1994, **6**, 439; K. Lahlil, A. Moradpour, C. Bowlas, F. Menou, P. Cassoux, J. Bonvoisin, J.-P. Launay, G. Dive and D. Dehareng, *J. Am. Chem. Soc.*, 1995, **117**, 9995.

9 J. Y. Becker, J. Bernstein, A. Ellern, H. Gershtenman and V. Khodorkovsky, *J. Mater. Chem.*, 1995, **5**, 1557.

10 A. E. Underhill, *J. Mater. Chem.*, 1992, **2**, 1.

11 Y. Yamashita, S. Tanaka, K. Imaeda, H. Inokuchi and M. Sano, *J. Org. Chem.*, 1992, **57**, 5517.

Received, 8th March 1996; Com. 6/01795I