An Extended Nickel Dithiolene Complex: Molecular Electronic Materials Based on Planar Bimetallic Subunits

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The species $Ni_2C_2S_4\{S_2C_2S_2C_2(CO_2Me)_2\}_2$, a new type of molecular electronic component, forms in good yield *via* two oxidation steps from $[Ni\{S_2C_2S_2C_2(CO_2Me)_2\}_2]^{2-}$; the extended planar structure of the intermediate $[Ni_2C_2S_4\{S_2C_2S_2(CO_2Me)_2\}_2]^{2-}$ was confirmed crystallographically.

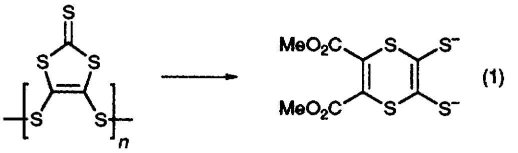
Research on molecular electrical conductors is dominated by studies on planar organic and metal-organic compounds.[1] Partial oxidation of many such species gives low-dimensional arrays of these donors providing an effective pathway for electronic conduction. Representative percursor species are the substituted tetrathiafulvalenes and the related metallodithiolenes. This communication concerns a new family of molecular electronic components based on planar bimetallic dithiolene building blocks.

Study of metallodithiolenes has been greatly invigorated by the introduction of new conductive and superconductive materials derived from the ligand $C_3S_5^{2-}$ (dmit).[2] These developments followed soon after Steimecke *et al.*[3] described convenient procedures for the isolation of $C_3S_5^{2-}$ derivatives obtained by the chemical reduction of carbon disulfide. We have found $C_3S_5^{2-}$ to be a versatile precursor to several new binary carbon sulfides.[4,5] These studies led us to examine metal complexes derived from the cyclic dithiolate $S_2C_2S_2C_2(CO_2Me)_2^{2-}$, which we prepared in two steps from $(C_3S_5)_n$ according to eqn. (1).[6]

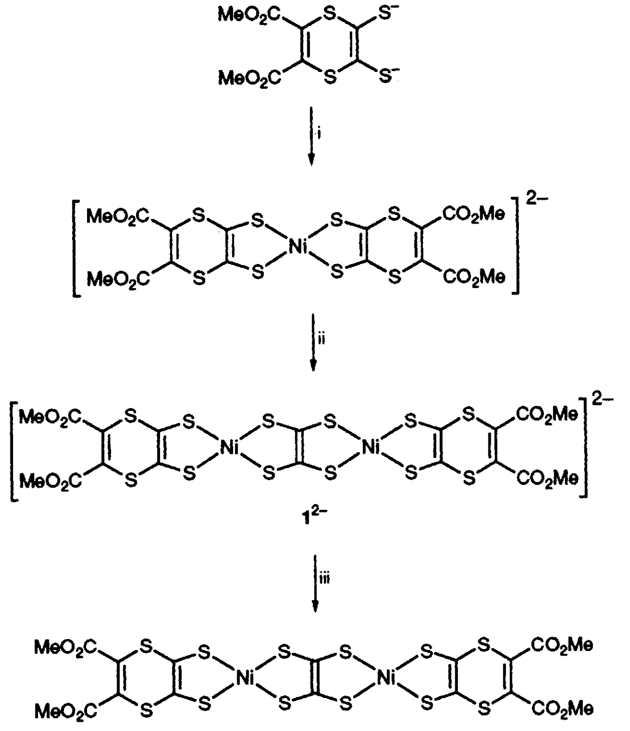
Solutions of nickel(II) salts react readily with solutions of $S_2C_2S_2C_2(CO_2Me)_2^{2-}$ to give dark green solutions which upon treatment with NEt_4Cl precipitate the salt $(NEt_4)_2[Ni\{S_2C_2S_2C_2(CO_2Me)_2\}_2]$.† The yield of analytically pure material was 85% after extraction into MeCN and evaporation. The stoichiometry was supported by ^1H NMR spectroscopy which showed only signals for the methyl ester and the counter cation consistent with a diamagnetic square-planar nickel complex.[7]

Solutions of $[Ni\{S_2C_2S_2C_2(CO_2Me)_2\}_2]^{2-}$ are very air sensitive. Acetonitrile solutions were found to oxidize in air as signaled by a colour change from green to purple-brown to give $(NEt_4)_2[Ni_2C_2S_4\{S_2C_2S_2C_2(CO_2Me)_2\}_2]$ [$(NEt_4)_2$ **1**], Scheme 1. This oxidation affects half of the initial $S_2C_2S_2C_2(CO_2Me)_2^{2-}$ ligands, one of which is degraded to tetrathiooxalate. The same conversion can also be conducted in slightly greater overall efficiency without isolation of the intermediate bis(dithiolene) complex. A typical experiment involves initial reaction of $OCS_2C_2S_2C_2(CO_2Me)_2$ (500 mg) and NaOMe (177 mg in 10 cm^3 MeOH), followed by addition of $[Ni(H_2O)_6]Cl_2$ (184 mg), and finally NEt_4Cl (420 mg) to give 215 mg of purple-brown microcrystals after recrystallization from MeCN and Et_2O in air. In this way we also prepared the NBu_4^+ and $AsPh_4^+$ salts of $\mathbf{1}^{2-}$, which were also obtained in analytical purity.

The structure of $(AsPh_4)_2$ **1** was determined by single-crystal X-ray diffraction.‡ The centrosymmetric anion (Fig. 1) features a pair of square-planar Ni centres interconnected by tetrathiooxalate. The striking aspect of the compound is the planar core which extends a length of 14.9 Å from S(6) to S(6′). The complex is terminated by alkenediesters which are bent away from the central $Ni_2C_6S_{12}$ plane through folding of the pairs of sulfur atoms in the 1,4-C_4S_2 (dithiin) rings.



(1)



Scheme 1 *Reagents and conditions:* i, 0.5 equiv. $[Ni(H_2O)_6]Cl_2$, MeOH, 5 min then 1 equiv. NEt_4 Br; ii, in MeCN O_2, 24 h, precipitation with Et_2O; iii, in MeCN, 2 equiv. $[Fe(C_5H_5)_2]^+$.

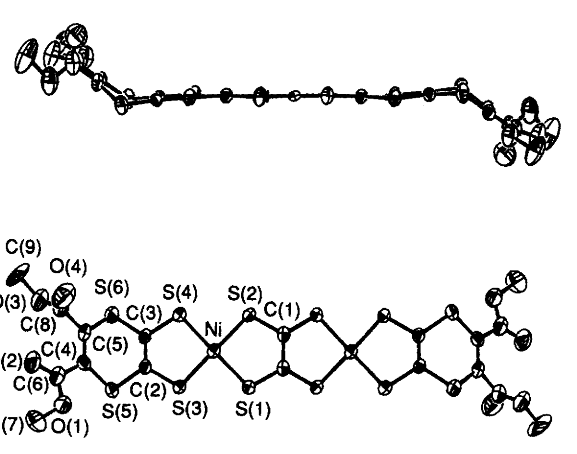


Fig. 1 Two views of the dianion in $(AsPh_4)_2[Ni_2C_2S_4\{S_2C_2S_2C_2(CO_2Me)_2\}_2]$. Hydrogen atoms are removed for clarity. Selected distances: Ni–S(1) 2.160(2), Ni–S(2) 2.154(2), Ni–S(3) 2.147(2), Ni–S(4) 2.158(2), S(2)–C(1) 1.701(6), C(1)–C(1) 1.427(8), C(2)–C(3) 1.334(10), C(2)–S(3) 1.728, C(2)–S(5) 1.749(7) Å.

Dithiins are formally 8π electron entities and the 1,4-derivatives are generally found to be folded along the S···S vector, although the energy barrier for planarization has been calculated[8] to be of the order of only a few kcal mol^{-1}.

Assignment of integral oxidation states in $\mathbf{1}^{2-}$ is ambiguous since the metal d orbitals are of comparable energy to the π molecular orbitals of the C_2S_4 fragment.[9] Nonetheless an effective oxidation state can be inferred from the carbon–carbon distance (d_{CC}) in the central C_2S_4 fragment.[10,11] A reference value of d_{CC} is that in ionic $C_2S_4^{2-}$ as seen in the $(NEt_4)_2C_2S_4$ [d_{CC} = 1.516(6) Å], whereas here the two mutually orthogonal CS_2^- fragments are connected by a C–C single bond.[11] A similar C–C distance is seen for $C_2S_4[Cu(PPh_3)_2]_2$, which does have a planar C_2S_4 core with d_{CC} = 1.53 Å.[12] At the other extreme, tetrathia-substituted olefins feature far shorter d_{CC} values. An internal standard for such a d_{CC} is the C(2)–C(3) distance for the *terminal* dithiolene chelates in $\mathbf{1}^{2-}$ of 1.334(10) Å. The d_{CC} value for the *central* C_2S_4 unit in $\mathbf{1}^{2-}$ is 1.43 Å. This dictates a description intermediate between the Ni^{II}_2 and Ni^{III}_2 cases.

The magnetic moment of $\mathbf{1}^{2-}$ is 2.3 μ_B at 273 K which is substantially less than the 2.83 μ_B expected for two unpaired electrons. The moment decreases to *ca.* 1.0 μ_B as the sample is cooled to 40 K, indicative of antiferromagnetic coupling. The possibility of a low-lying triplet excited state is also indicated in Hoffmann's calculation on $[Ni_2(\mu\text{-}C_2S_4)H_4]^{2-}$.[11] This same model predicts that neutral $Ni_2C_2S_4X_4$ (X is a pseudohalide) should be diamagnetic.

The large cations in the salts of $\mathbf{1}^{2-}$ prevent significant electronic interactions between the bimetallic subunits in the solid state. Cyclic voltammetry on MeCN solutions of $\mathbf{1}^{2-}$ indicate $1e^-$ oxidations at 200 and 400 mV *vs.* Ag–AgCl.[13] These mild potentials prompted us to conduct the oxidation on a preparative scale. In a typical experiment a MeCN solution of $(NEt_4)_2\mathbf{1}$ (403 mg) was treated with 2 equivalents of $[Fe(C_5H_5)_2]PF_6$. The initially brown solution became forest green and 273 mg of $\mathbf{1}^0$ precipitated as a black-green analytically pure powder. The neutral product is soluble only in coordinating solvents (DMF, pyridine). The absence of counter ions was also confirmed by the ^1H NMR spectrum of a $[^2H_5]$pyridine solution which displays only a single peak assigned to the methyl ester functionality. Broadening of the methyl peak is attributed to the binding of pyridine giving octahedral and hence magnetic Ni centres.

Pressed pellets of powdered $\mathbf{1}^0$ display electrical conductivity (two point) of 10^{-3} ohm^{-1} cm^{-1}. This conductivity, while not especially high compared to many charge-transfer salts,[1] is noteworthy for an undoped molecular solid. These results encourage further study specifically directed at single crystals of $\mathbf{1}^0$ and more generally aimed at new conductive materials based on planar $M_2C_2S_4$ building blocks. In this context it is very interesting that $(NiC_2S_4)_n$, an amorphous and insoluble polymeric substance, displays conductivities of 10^2 ohm^{-1} cm^{-1}.[14]

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Footnotes

† Analysis (CHNS) ^1H NMR (CD_3CN): 3.69 (12H, s), 3.22 (16H, br), 1.24 (24H, br)

‡ *Crystal data* for $(AsPh_4)_2$ **1**: $C_{66}H_{52}As_2Ni_2O_8S_{12}$, M = 1625.12) triclinic space group $P\bar{1}$, a = 9.9414(15), b = 10.4025(14), c = 17.9743(24) Å, α = 103.350(4), β = 98.825(5), γ = 92.123(5)°, U = 1782.1(8) Å^3, Z = 1, D_c = 1.514 g cm^{-3}, F(000) = 826 e/unit cell, μ = 18.38, crystal size = 0.1 × 0.2 × 0.4 mm. 5479 Intensities ($3 < 2\theta < 46°$) were recorded using a Syntex $P2_1$ diffractometer equipped with a Crystallogic automation. The structure was solved by direct methods (SHELX-76) and refined by least-squares Fourier calculations. 2155 Observed reflections, $I > 2.5\sigma(I)$, non-hydrogen atoms refined anisotropically to final agreement factors of R = 0.035 and R_w = 0.047. The anion is centrosymmetric.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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