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FULL PAPER

A new family of sulfur-rich ligands based on the dmit system: synthesis and metal complexation of 4–4′-covalently bridged bis(2-thioxo-1,3-dithiol-5-thiolato) units

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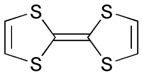
The synthesis of a new series of sulfur-rich ligands is reported. These compounds, which are related to the dmit^{2-} (2-thioxo-1,3-dithiol-4,5-dithiolato) structure, comprise two 2-thioxo-1,3-dithiol-5-thiolato units linked by a bridging unit at the 4-position of the heterocycle *via* a dithioether spacer unit. Complexation reactions have been carried out on a variety of metal centres; dialkyl tin and gold(I) derivatives have been isolated and fully characterised. The X-ray crystal structure of an octahedral Ni(II) complex, involving two coordinating pyridine molecules, is presented.

Introduction

The conducting and magnetic properties of molecular based materials are normally sustained by a high level of order in the bulk solid, orchestrated by a network of close intermolecular contacts. Highly chalcogenated species are particularly good at invoking such interactions through non-covalent X ··· Y bonds (X/Y = Group 16 atom). The most prevalent members of this family of materials are tetrathiafulvalene (TTF) **1**[1] and its derivatives, such as BEDT-TTF **2**, together with the metal dmit complexes $[M(dmit)_2]^{n-}$ **3** (dmit^{2-} = 2-thioxo-1,3-dithiol-4,5-dithiolato),[2] which form the basis of most of the known organometallic molecular conductors and superconductors.



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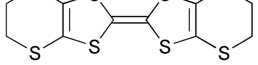

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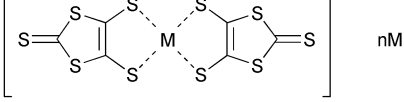

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In the case of the dmit^{2-} complexes **3**, previous work has been constrained to the variation of the transition metal and/or the counter-cation. The most common metal complexes contain Ni, Pd, Pt, Fe, Cu, Au or Rh, whereas the counterion (R in $R_n[M(dmit)_2]$) is typically H_4N^+, R_4N^+, R_4P^+, R_4As^+, or Me_3SO^+.[3] Conducting materials can be prepared either by electrocrystallisation to afford complexes with non-integral oxidation states ($R_n[M(dmit)_2]$, where n = non-integer) or by metathesis with a suitable electron donor molecule, such as TTF (*e.g.* in $[TTF][Pd(dmit)_2]_2$).[3] The function of the metal in the conducting mechanism is difficult to judge, but it is acknowledged that square planar complexes provide the best geometry for close intermolecular interactions. For this reason, Ni(II), Pd(II) and Pt(II) salts are *a priori* species for highly ordered materials containing stacks of planar complexes. The conducting behaviour of metal(dmit)$_2$ systems is dependent upon the solid-state structure: nickel salts form molecular stacks, in which the Ni ··· Ni separation is too great to foster a conducting channel through the metal sites,[4] whereas platinum gives rise to dimeric species.[5] The Group 10 metals also afford dmit complexes with different stoichiometries and crystal phases within the same complex, giving rise to materials with a range of conductivity values. Closed-shell counter-cations affect the packing motif of the heterocycles; for example, larger organic species (such as Bu_4N^+) restrict close packing of the metal(dmit)$_2$ species. Open shell cations, such as $TTF^{\bullet+}$, offer greater dimensionality to the conducting medium, since conductivity can also be manifested through the network of TTF units as well as the metal(dmit)$_2$ species. It is not surprising, therefore, that these hybrid systems exhibit high levels of conductivity. Indeed, $[TTF][Ni(dmit)_2]_2$,[6] α′-$[TTF][Pd(dmit)_2]_2$,[7] α-$[TTF][Pd(dmit)_2]_2$,[8] and α-$[EDT\text{-}TTF][Ni(dmit)_2]$[9] comprise four of the nine reported dmit-based superconductors.

Herein, we report on the synthesis and characterisation of a new family of dmit-related ligands **6**–**10**[10] together with studies of their complexation behaviour towards different metal centres. In contrast to the dmit^{2-} ligand, our target derivatives incorporate two thioether and two thiolate environments as the overall chelating species. The thioether functionalities are linked *via* suitable spacer groups and this feature should present a major advantage over traditional dmit^{2-} complexes, by adding

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solubility and structural and synthetic versatility to the overall nature of the complex. The X-ray crystal structure of an octahedral dithiolato nickel complex is also presented.

Owing to the large amount of investigative synthetic work carried out by many research groups, the applications of TTF derivatives are no longer confined to the preparation and study of conducting materials, but are extended towards other areas of materials science, such as sensors, liquid crystals, nonlinear optics, supramolecular switches and redox polymers.[11] Our route towards dmit-σ-dmit bridged ligands opens up an almost infinite number of synthetic variations. Furthermore, the spacer group can be designed to incorporate other features into the ligand, such as chirality, rigidity, additional chelating atoms and even other redox-active groups. With this type of design strategy, the role of metal dmits in materials science could also deviate from the traditional focus on the conducting and magnetic behaviour of these materials.

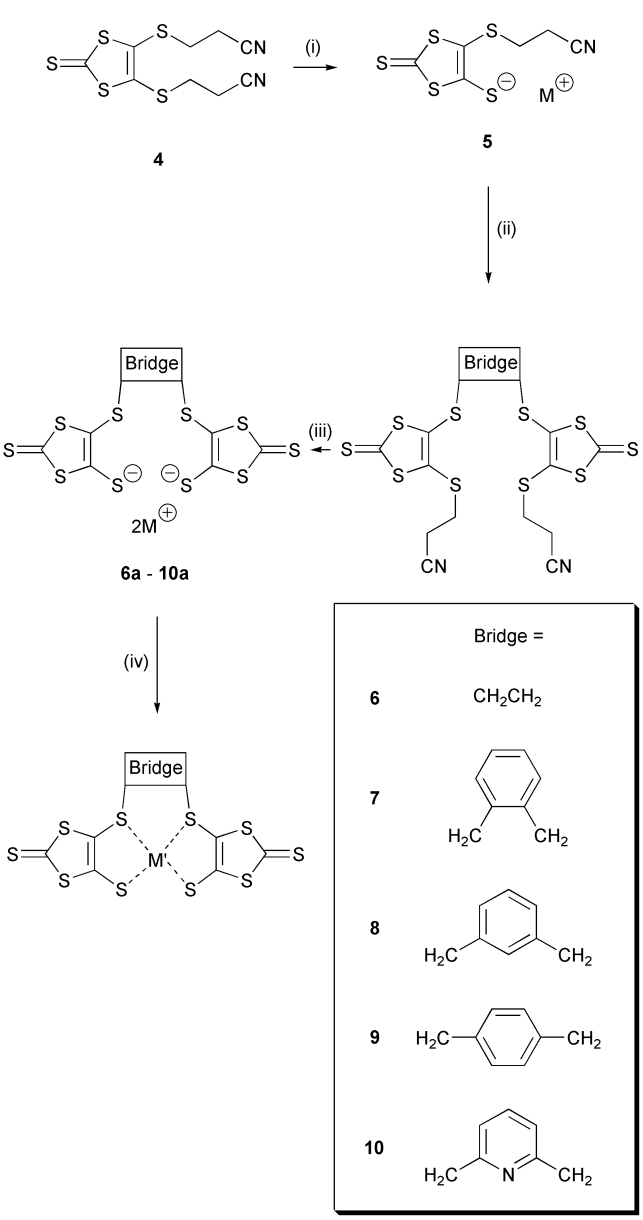
Results and discussion

Ligand synthesis

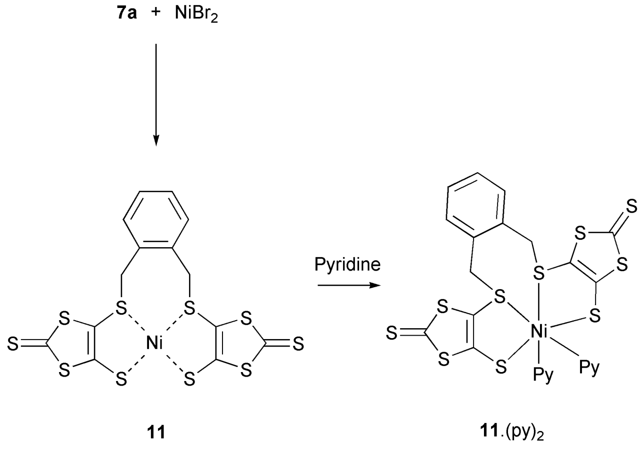
In general, our strategy involves the preparation of bis-(2-thioxo-1,3-dithiol-5-cyanoethylthio) derivatives **6**–**10** that are linked at the 4(4′)-positions of the sulfur heterocycles *via* a spacer group. These new ligands can be prepared from the reaction of compound **4**[12] with one equivalent of base, followed by the addition of a suitable difunctional bridging unit (Scheme 1). Mono-deprotected intermediate **5** is stable in solution (under N_2) for several days, but is typically treated with a half molar equivalent of dibromo compound immediately, affording the corresponding bridged systems **6**–**10**. Thus, compounds **6**–**9** were obtained from the reaction of **5** with 1,2-dibromoethane (70%), 1,2-bis(bromomethyl)benzene (75%), 1,3-bis(bromomethyl)benzene (65%) and 1,4-bis(bromomethyl)benzene (60%) respectively. The pyridine derivative **10**, obtained as a crude oil from the reaction of **5** and 2,6-bis(bromomethyl)pyridine (50%), was converted into the analytically pure salt **10**·HCl by treatment with acetyl chloride/ethanol at 0 °C in ethyl acetate (80% from **10**). Under mildly basic conditions compounds **6**–**10** can be easily deprotected producing dithiolate salts **6a**–**10a** (Scheme 1), affording strong ligands for complexation to transition metal species. The bis(tetramethyl ammonium) salt of thiolate **6a** was isolated and found to be stable under ambient conditions for several weeks,[13] but in general dithiolates **6a**–**10a** were treated *in situ* with metal salts (*vide infra*). Using this methodology, we are presented with a vast range of possible derivatives due to the abundance of available difunctional systems that are capable of undergoing nucleophilic substitution reactions with a thiolate functionality.

Direct metallation of thiolate ligands

Treatment of thiolate ligands **6a**–**10a** with metal chlorides or bromides MX_2 (M = Fe, Co, Ni, Cu, Zn), gave impure coloured solids, most of which were sparingly soluble in common organic solvents or water. We were not able to purify the complexes to give satisfactory elemental analyses and some of the compounds showed signs of decomposition by a series of colour changes on standing. Only in one case, the reaction of *o*-xylene bridge ligand **7a** with nickel bromide (Scheme 2), were we able to characterise the product (**11**). The room temperature magnetic moment of **11** (3.33 μ_B) is typical of a tetrahedrally-distorted nickel(II) species.[14] Complex **11** is soluble in DMSO, and sparingly soluble in DMF or pyridine. Recrystallisation of **11** from pyridine afforded small black crystals of the complex **11**·$(py)_2$, in which two molecules of pyridine have coordinated to the nickel centre producing an octahedral species. The X-ray structure of $[Ni(dmit\text{–}o\text{-}CH_2C_6H_4CH_2\text{–}dmit)(py)_2]$ (Fig. 1, Table 1) displays a distorted octahedral coordination geometry around the metallic centre with one of the pyridine ligands and one of the thioether groups in the apical positions. The main distortion arises from the pinching of the S–Ni–S angles of the coordinating dmit as commonly seen when in a non-square planar geometry. The Ni–S distances range from 2.3842(17) to 2.5827(18) Å, with the Ni–S(thioether) distances greater than the respective Ni–S(thiolate) bond lengths. The distances within



Scheme 1 Reagents and conditions: (i) R_4NOH, THF (ii) 1/2 equiv. Br–*bridge*–Br; (iii) R_4NOH or NaOEt, THF or DMF; (iv) metal halide.



Scheme 2

Table 1 Selected bond lengths [Å] and angles [°] for **11**·(py)$_2$

Ni(1)–N(1)	2.095(5)	S(5)–C(2)	1.712(6)
Ni(1)–N(2)	2.109(5)	S(5)–C(3)	1.741(5)
Ni(1)–S(10)	2.3842(17)	S(3)–C(2)	1.734(6)
Ni(1)–S(1)	2.4105(17)	S(3)–C(1)	1.757(5)
Ni(1)–S(2)	2.5585(17)	S(9)–C(13)	1.737(7)
Ni(1)–S(6)	2.5827(18)	S(9)–C(14)	1.752(5)
S(1)–C(1)	1.717(6)	S(7)–C(13)	1.711(7)
S(2)–C(3)	1.749(5)	S(7)–C(12)	1.757(6)
S(2)–C(4)	1.841(6)	S(4)–C(2)	1.644(6)
S(10)–C(14)	1.714(6)	S(8)–C(13)	1.659(6)
S(6)–C(12)	1.743(6)	C(3)–C(1)	1.351(8)
S(6)–C(11)	1.835(7)		
N(1)–Ni(1)–N(2)	96.17(19)	S(10)–Ni(1)–S(6)	85.05(6)
N(1)–Ni(1)–S(10)	94.61(13)	S(1)–Ni(1)–S(6)	92.31(6)
N(2)–Ni(1)–S(10)	87.79(13)	S(2)–Ni(1)–S(6)	98.32(6)
N(1)–Ni(1)–S(1)	87.01(13)	C(1)–S(1)–Ni(1)	98.20(19)
N(2)–Ni(1)–S(1)	94.88(13)	C(3)–S(2)–Ni(1)	96.9(2)
S(10)–Ni(1)–S(1)	176.71(7)	C(4)–S(2)–Ni(1)	109.7(2)
N(1)–Ni(1)–S(2)	171.09(13)	C(14)–S(10)–Ni(1)	100.5(2)
N(2)–Ni(1)–S(2)	83.39(14)	C(12)–S(6)–Ni(1)	97.7(2)
S(10)–Ni(1)–S(2)	94.26(6)	C(11)–S(6)–Ni(1)	121.5(2)
S(1)–Ni(1)–S(2)	84.16(5)	C(19)–N(1)–Ni(1)	120.6(4)
N(1)–Ni(1)–S(6)	83.23(15)	C(15)–N(1)–Ni(1)	122.7(4)
N(2)–Ni(1)–S(6)	172.75(13)	C(24)–N(2)–Ni(1)	120.5(4)

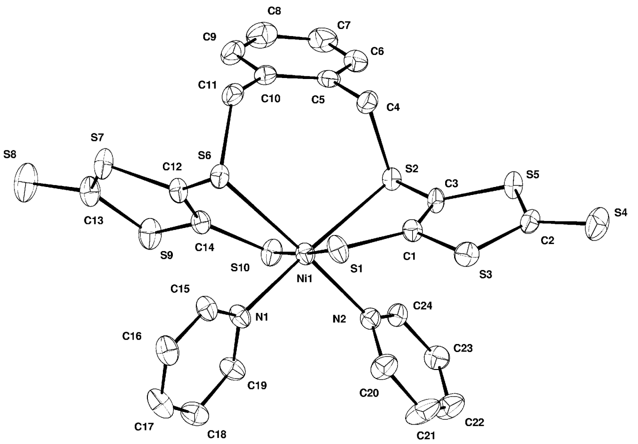


Fig. 1 X-Ray crystal structure of **11**·(py)$_2$ (H atoms omitted for clarity).

the dmit unit (S–C 1.736 Å on average and C=C 1.351(8), 1.340(8) Å) are similar to those found in the [Ni(C$_3$S$_5$)$_2$] unit.[4] The Ni–N bond lengths (2.095(5) and 2.109(5) Å) are similar to those found in related nickel thioether complexes with pyridine as additional ligands.[15–17] The angle between the least squares planes of the two pyridine rings is 53.89(26)°.

Interestingly, the molecules form chains running along the *a* axis *via* weak S ··· S interactions within the sum of the van der Waals radii (S5–S7 = 3.418(3), S5–S6 = 3.521(4) Å) (Fig. 2).

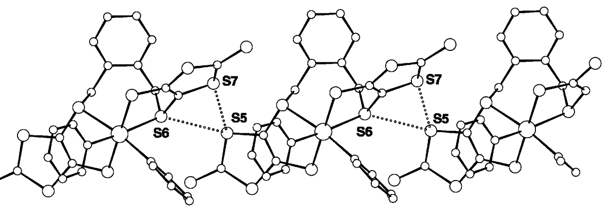
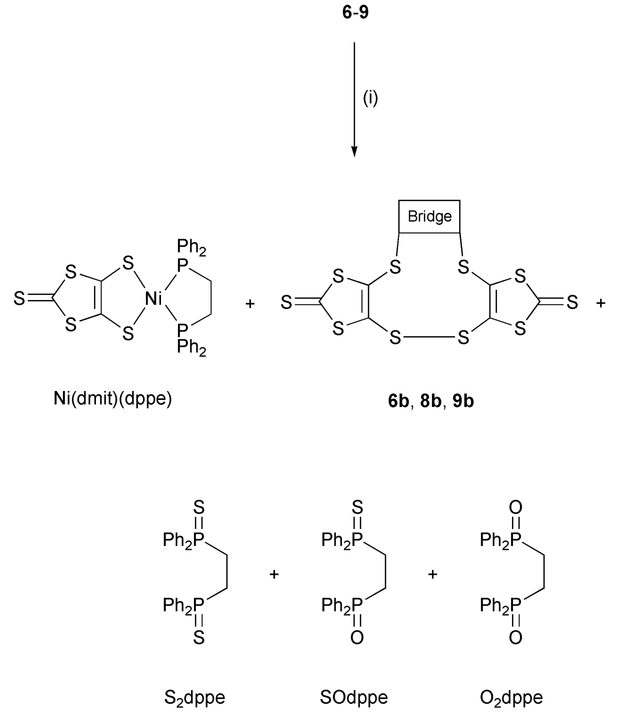


Fig. 2 Chains extending along the *a* axis of **11**·(py)$_2$.

Despite the non-planar geometry of the complex (*cf.* typical square planar metal-dmit$_2$ systems), this feature indicates that such materials can display long-range order through short intermolecular S ··· S contacts, which satisfies one criterion for a material with conducting properties.

In order to improve the solubility of the complexes, we carried out the reaction of the dithiolate derivatives **6a**–**9a** with the nickel(II) complex [NiCl$_2$dppe] (dppe = bis(diphenylphosphino)ethane). This reaction gave a mixture of products (Scheme 3) which were purified by column chromatography and identified by NMR and mass spectroscopy. The corresponding metallic bis-dithiolate compound, bridged by the spacer unit, was not obtained from any of the experiments performed. Instead, we identified [Ni(dmit)dppe][18] as the major product (as a result of the cleavage of the spacer unit), together with cyclic compounds **6b**, **8b** and **9b**, presumably from the oxidation of the thiolate functionalities followed by radical coupling. Similar S–S bond formation was previously described by some of us in the reaction of [Sn(dmit)Me$_2$] with [Ni(Mes)Br(PPh$_2$Me)$_2$].[19] Additionally, some derivatives of the diphosphine were also detected: the dioxide and disulfide of bis(diphenylphosphino)ethane (O$_2$dppe and S$_2$dppe), were identified by comparison of their spectroscopic properties with pure samples; on the basis of ^{31}P NMR and mass spectra we identified diphenylphosphineoxide(diphenylphosphinesulfide)ethane (SOdppe).

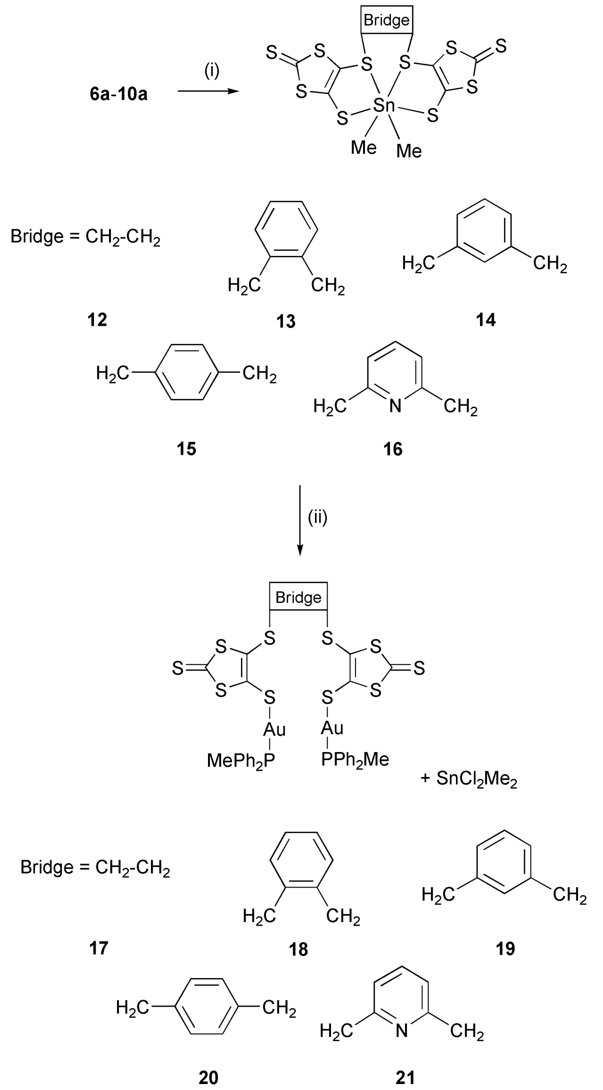


Scheme 3 Reagents and conditions: (i) NaOEt, [NiCl$_2$(dppe)].

Transmetallation reactions of thiolates

Since the synthesis of metal complexes starting directly from the dithiolate species **6a**–**10a** proved problematical, we decided to investigate the use of tin derivatives as dithiolate transfer reagents. We pursued this approach because similar dithiolate tin complexes have shown that they can easily transfer the dithiolate ligand to other metals.[20] The dithiolate species **6a**–**10a** were treated with [SnCl$_2$Me$_2$] according to Scheme 4. The resulting tin compounds **12**–**16** can be isolated as yellow air-stable solids which are insoluble in most organic solvents (14–97% yield from **6a**–**10a**).

The ^{1}H NMR spectra of **12**–**16** in d$_6$-DMSO show the corresponding peaks due to the spacer units and the signals due to the methyl groups co-ordinated to the metallic centre. These occur as multiplets in **12**, **15** and **16**, two singlets in the case of **13** and **15** and a unique signal flanked by tin satellites for compound **14**. In all cases the mass spectra (LSIMS$^+$) do not show the molecular ion peak; instead, fragmentation peaks



Scheme 4 Reagents and conditions: (i) $[\mathrm{SnCl_2Me_2}]$; (ii) $2[\mathrm{AuCl(PPh_2Me)}]$.

are observed due to the cleavage of the spacer units to give $[\mathrm{Sn(dmit)Me_2}]^+$ species.

Tin dithiolates act as good transfer reagents with gold(I) and gold(III)[20] complexes under very mild conditions. The dialkyl tin analogues of **12**–**16** are, therefore, suitable reagents for the reaction with gold(I) species. Complexes **17**–**21** with the formula $[\mathrm{Au_2(dmit{-}bridge{-}dmit)(PPh_2Me)_2}]$ (Scheme 4) can be isolated as air and moisture stable yellow solids which are soluble in common organic solvents. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$NMR spectra display a singlet at about 22 ppm assignable to only one type of phosphorus. The ^{1}H NMR spectra show multiplets in the phenyl region due to the $\mathrm{PPh_2Me}$ phosphine and the aromatic groups in **18**–**21**. For complex **17**, a singlet centred at 2.99 ppm is assignable to the $\mathrm{SCH_2CH_2S}$ fragment. In all cases, a doublet at *ca.* 2 ppm is observed, corresponding to the methyl group of the $\mathrm{PPh_2Me}$ unit coupled with the phosphorus atom. In the IR spectra of compounds **17**–**21**, the ν(C=S) vibration appears at about 1060 and 1020 cm^{-1}, which is similar to those found in other dmit-gold derivatives.[21]

Complexes **17**, **18** and **21** show the parent peak in LSIMS$^+$ (nba as matrix) with low abundance. In addition $[\mathrm{S(AuPPh_2Me)_3}]^+$ and $[\mathrm{S(AuPPh_2Me)_2}]^+$ are also present in all cases, as a consequence of the decomposition of the dmit fragments.

On the basis that the tin derivatives are good transfer reagents for the preparation of gold(I) complexes, we performed the reaction of compounds **12**–**16** with the nickel complex $[\mathrm{NiCl_2(dppe)}]$ in order to transfer the dithiolate ligand to the Ni(II) centre. Nevertheless, the reactions proceeded in the same way as those using the dithiolates **6a**–**9a**, though higher yields were obtained for cyclic derivatives **6b**, **8b** and **9b**.

Conclusion

We have presented the synthesis of a new series of sulfur-based ligands as variants of the well-known dmit^{2-} system. The methodology used for the synthesis of the ligands opens up a plethora of structural possibilities within the bridging fragment. The incorporation of functional groups and more complex species should be readily accessible. Attempts at forming transition metal complexes directly from dithiolated species mostly resulted in poorly soluble, unstable and impure products. Nevertheless, dialkyl tin derivatives have been successfully isolated, which have potential use in transmetallation reactions. For example, gold(I) complexes have been prepared by this route. The major challenge ahead is to design and synthesise similar ligands with enhanced solubility, enforcing stability and square planar geometry in the resulting transition metal complexes.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 883 and ATI Mattson Instruments Genesis Series spectrophotometer, over the range 4000–200 cm^{-1}, by using Nujol mulls between polyethylene sheets or as KBr discs. ^{1}H and ^{31}P NMR spectra on a Varian UNITY 300 or Bruker AC 250 in $\mathrm{CDCl_3}$ or $[\mathrm{D_6}]$DMSO solutions; chemical shifts are quoted relative to $\mathrm{SiMe_4}$ (^{1}H) and $\mathrm{H_3PO_4}$ (external ^{31}P). The C, H, N and S analyses were performed with a Perkin-Elmer 2400 microanalyser and also by MEDAC Ltd. Mass spectra were recorded on a VG Autospec, by liquid secondary ion mass spectrometry (LSIMS$^+$) using nitrobenzylalcohol as matrix and a caesium gun or using a VG 7070E in EI or FAB mode. Absorption spectra were obtained using a Unicam UV2 spectrophotometer. The melting points were measured using Gallenkamp or Electrothermal apparatus.

Flash column chromatography was carried out using Fluka Kiesselgel (70–230 mesh). Most of the reactions were performed under a nitrogen atmosphere. $(\mathrm{NEt_2})_2[\mathrm{Zn(dmit)_2}]$,[22] $[\mathrm{AuCl(PPh_2Me)}]$,[23] $[\mathrm{NiCl_2(dppe)}]$[24] were obtained according to the literature procedures. All solvents were dried and distilled prior to use, using standard literature procedures. All organic reagents were used as supplied.

Syntheses

General procedure for the synthesis of compounds 6–10. To a stirred solution of **4**[12] (2.0 g, 6.57 mmol) in THF (40 ml), at −5 °C, was added tetrabutylammonium hydroxide (7.9 ml, 1 M solution in methanol, 7.90 mmol) over 20–30 min. To the resulting purple mixture was added 1,2-dibromoethane, α′α-dibromo-*o*-xylene, α′α-dibromo-*m*-xylene, α′α-dibromo-*p*-xylene or 2,6-bis(bromomethyl)pyridine (0.6 eq.). The reaction was allowed to stir at room temperature for 16 h. The solvent was evaporated under reduced pressure and the residue chromatographed on silica gel using dichloromethane as the eluent.

3-(5-{2-[5-(2-Cyanoethylsulfanyl)-2-thioxo-1,3-dithiol-4-ylsulfanyl]ethylsulfanyl}-2-thioxo-1,3-dithiol-4-ylsulfanyl)propionitrile (6). Yellow powder, recrystallised from acetonitrile. Yield 70%. mp 125–126 °C. MS (EI, M$^+$): *m*/*z*: 528. ^{1}H NMR (250 MHz, $[\mathrm{D_6}]$DMSO, 25 °C) δ 3.31 (s, 4H), 3.26 (t, 4H, J = 6.5 Hz) and 2.95 (t, 4H, J = 6.5 Hz). ^{13}C NMR (63 MHz, $[\mathrm{D_6}]$DMSO, 25 °C) δ 210.8, 137.6, 135.5, 118.8, 35.7, 31.5 and 18.2. IR (cm^{-1}) 2245 (C≡N), 1050 (C=S). Elemental anal. Calc. for $\mathrm{C_{14}H_{12}N_2S_{10}}$ C, 31.8; H, 2.3; N, 5.3%. Found: C, 31.9; H, 2.2; N, 5.4%.

3-(5-{2-[5-(2-Cyanoethylsulfanyl)-2-thioxo-1,3-dithiol-4-ylsulfanylmethyl]benzylsulfanyl}-2-thioxo-1,3-dithiol-4-ylsulfanyl)propionitrile (7). Orange/red oil. Yield 75%. MS (EI, M$^+$): *m*/*z*:

604. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C) δ 7.29 (m, 4H), 4.29 (s, 4H), 2.95 (t, 4H, J = 6.95 Hz) and 2.57 (t, 4H J = 6.95 Hz). ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C) δ 210.5, 139.0, 136.2, 134.5, 131.6, 129.4, 117.8, 39.1, 32.4 and 19.1. Elemental anal. Calc. for $C_{20}H_{16}N_2S_{10}$ C, 39.7; H, 2.7; N, 4.6%. Found: C, 39.9; H, 2.6; N, 4.6%.

*3-(5-{3-[5-(2-Cyanoethylsulfanyl)-2-thioxo-1,3-dithiol-4-ylsulfanylmethyl]benzylsulfanyl}-2-thioxo-1,3-dithiol-4-ylsulfanyl)-propionitrile (**8**).* Orange/red oil. Yield 65%. MS (FAB, M$^+$): *m*/*z*: 605. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C) δ 7.33 (m, 4H), 4.10 (s, 4H), 2.99 (t, 4H, J = 7.01 Hz) and 2.61 (t, 4H J = 6.89 Hz). ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C) δ 210.6, 140.1, 137.0, 134.1, 130.0, 129.3, 117.7, 41.1, 32.4 and 19.1.

*3-(5-{4-[5-(2-Cyanoethylsulfanyl)-2-thioxo-1,3-dithiol-4-ylsulfanylmethyl]benzylsulfanyl}-2-thioxo-1,3-dithiol-4-ylsulfanyl)-propionitrile (**9**).* Yellow powder, recrystallised from acetonitrile. Yield 60%. mp 120–121 °C. ^{1}H NMR (250 MHz, [D$_6$]DMSO, 25 °C) δ 7.35 (s, 4H), 4.26 (s, 4H), 3.15 (t, 4H, J = 6.70 Hz) and 2.83 (t, 4H J = 6.70 Hz). ^{13}C NMR (63 MHz, [D$_6$]DMSO, 25 °C) δ 210.9, 138.8, 136.1, 135.2, 129.4, 118.8, 40.0, 31.5 and 18.1. IR (cm^{-1}) 2250 (C≡N), 1065 (C=S). Elemental anal. Calc. for $C_{20}H_{16}N_2S_{10}$ C, 39.7; H, 2.7; N, 4.6%. Found: C, 39.9; H, 2.8; N, 4.9%.

*3-(5-{6-[5-(2-Cyanoethylsulfanyl)-2-thioxo-1,3-dithiol-4-ylsulfanylmethyl]pyridin-2-ylmethylsulfanyl}-2-thioxo-1,3-dithiol-4-ylsulfanyl)propionitrile hydrochloride (**10·HCl**).* Compound **10** was isolated as the hydrochloride salt as a yellow solid: following the general procedure given above, compound **10** was then dissolved in ethyl acetate. A solution of HCl in ethyl acetate (prepared by mixing equimolar amounts of acetyl chloride and ethanol at 0 °C) was added to precipitate the product. Overall yield 40%. mp 154–155 °C. ^{1}H NMR (250 MHz, [D$_6$]DMSO, 25 °C) δ 7.90 (t, 1H, J = 7.74 Hz), 7.46 (d, 2H, J = 7.72 Hz), 6.89 (br s, 1H), 4.34 (s, 4H), 3.17 (t, 4H J = 6.80 Hz) and 2.86 (t, 4H J = 6.80 Hz). ^{13}C NMR (63 MHz, [D$_6$]DMSO, 25 °C) δ 219.0, 155.6, 139.2, 138.0, 136.0, 122.9, 118.7, 31.5 and 18.2. IR (cm^{-1}) 2246 (C≡N), 1060 (C=S). Elemental anal. Calc. for $C_{19}H_{16}N_3ClS_{10}$ C, 35.5; H, 2.5; N, 6.5%. Found: C, 35.9; H, 2.5; N, 6.5%.

*Bis(tetramethylammonium) salt (**6a**).* To a stirred solution of **6** (0.5 g, 0.945 mmol) in dry THF (20 ml) was added tetramethylammonium hydroxide (0.72 ml of a 25% w/w solution in methanol, 1.98 mmol), dropwise over 10 min to give a red solution. After 30 min, the resulting precipitate was isolated by filtration and washed with dry THF, followed by dry diethyl ether, to give an orange powder. Yield: 0.52 g (96%), recrystallised from methanol, mp 165 °C (decomp.). ^{1}H NMR (250 MHz, [D$_6$]DMSO, 25 °C) δ 3.12 (s, 24H) and 3.01 (s, 4H). ^{13}C NMR (63 MHz, [D$_6$]DMSO, 25 °C) δ 210.9, 171.7, 110.4, 54.5 and 34.2. IR (cm^{-1}) 1058 (C=S).

*2,3,5,7,9,12,14,16-Octathia-tricyclo[11.3.0.0^{4,8}]hexadeca-1-(13),4(8)-diene-6,15-dithione (**6b**).*

Method (a). To a suspension of compound **6** (0.10 g, 0.19 mmol) in THF (10 ml) was added a solution of 0.1 M NaOEt (0.4 mmol; 4 ml) and to the resulting red solution, [Ni Cl_2(dppe)] (0.10 g, 0.19 mmol) was added. After stirring for 12 hours, the red solution became brown and the solvent was removed *in vacuo*. The crude product was purified by column chromatography using hexane/acetone (2 : 1). Yield for [Ni(dmit)(dppe)]: 76% (based on [NiCl_2(dppe)]). The organic compound **6b** was obtained in very small quantity, 3% overall, as a yellow oil.

Method (b). To a suspension of **12** (0.10 g, 0.18 mmol) in dried acetone (10 ml) was added [NiCl_2(dppe)] (0.095 g, 0.18 mmol). After stirring for 12 hours, the suspension became a brown solution and the solvent was removed *in vacuo*. The crude product was purified as above. Yield for [Ni(dmit)(dppe)]: 93% (based on [NiCl_2(dppe)]). The organic compound **6** was obtained in 11% overall yield as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.31 (s, 4 H, SCH_2CH_2S).

***8b**. Method (a).* The reaction was performed in a similar way as the previous one. Starting from **8** (0.10 g, 0.16 mmol) in THF (10 ml) a solution of 0.1 M NaOEt (0.4 mmol; 4 ml) was added and to the resulting red solution, [NiCl_2(dppe)] (0.0845 g, 0.16 mmol) was added. After stirring for 12 hours, the red solution became brown and the solvent was removed *in vacuo*. Yield for [Ni(dmit)(dppe)]: 82% (based on [NiCl_2(dppe)]). The organic compound **8b** was obtained in very small quantity, 3% overall, as a yellow oil.

Method (b). To a solution of **14** (0.10 g, 0.15 mmol) in distilled THF (10 ml) was added [NiCl_2(dppe)] (0.0792 g, 0.15 mmol). After stirring for 12 hours, the orange solution became brown and the solvent was removed *in vacuo*. The crude product was purified by column chromatography using hexane–acetone (1 : 1). Yield for [Ni(dmit)(dppe)]: 84% (based on [NiCl_2(dppe)]). The organic compound **8b** was obtained in 10% overall yield as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.73–7.69 (m, 2 H, Ph), 7.57–7.52 (m, 2 H, Ph) and 4.28–4.16 (m, 4 H, SCH_2).

***9b**.* To a suspension of compound **9** (0.10 g, 0.15 mmol) in 10 ml of THF was added [NidppeCl_2] (0.0792 g, 0.15 mmol). After stirring for 12 hours, the suspension became a brown solution and the solvent was removed *in vacuo*. The crude product was purified by column chromatography using ether–dichloromethane (1 : 1). Yield for [Ni(dmit)(dppe)]: 78% (based on [NiCl_2(dppe)]). The organic compound **9b** was obtained in 21% overall yield as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.73–7.69 (m, 2 H, Ph), 7.56–7.51 (m, 2 H, Ph) and 4.24–4.21 (m, 4 H, SCH_2).

[Ni(dmit-*o*-$CH_2C_6H_4CH_2$-dmit)(py)$_2$] (11·(py)$_2$). Under N_2 to a stirred solution of compound **7** (0.50 g, 0.80 mmol) in 10 ml of THF was added NaOEt (0.124 g, 1.8 mmol) in 5 ml of dry distilled ethanol to yield a dark red solution. After stirring for 20 minutes at room temperature, a solution of $NiBr_2$ (0.175 g, 0.80 mmol) in 5 ml of dry ethanol was added to yield a dark brown solution and brown precipitate. The precipitate was filtered off, and washed sequentially with 20 ml ethanol, 20 ml deionised water and 20 ml propan-2-ol to yield 0.260 g of brown powder. The brown powder was dissolved in 15 ml pyridine to give a brown/black solution and after 3 days several small black crystals of **11**·(py)$_2$ formed at the surface of the pyridine.

*Crystal data for **11**·(py)$_2$.* Data were collected on a Bruker Nonius Kappa CCD area detector diffractometer with a rotating molybdenum anode following standard procedures. Crystal data: $C_{24}H_{18}N_2NiS_{10}$, M_r = 713.71, T = 298(2) K, triclinic, space group $P\bar{1}$, a = 9.5662(6), b = 12.5254(8), c = 14.0131(8) Å, α = 76.558(3), β = 86.314(3), γ = 67.969(3)°, V = 1513.32(16) Å^3, ρ_{calc} = 1.566 g cm^{-3}, μ = 1.350 mm^{-1}, Z = 2, reflections collected: 18864, independent reflections: 4319 (R_{int} = 0.1189), final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0517, $wR2$ = 0.1149, R indices (all data): $R1$ = 0.1009. $wR2$ = 0.1364.

CCDC reference number 181362.

See http://www.rsc.org/suppdata/dt/b2/b201615j/ for crystallographic data in CIF or other electronic format.

General procedure for the synthesis of dimethyl tin derivatives 12–16. To a suspension or solution of the corresponding protected dithiolate (**6**–**10**, 0.33 mmol) in THF (10 ml) was added a solution of NaOEt (6.6 ml, 0.1 M, 0.66 mmol) and to the resulting red solution, [SnCl_2Me_2] (0.0725 g, 0.33 mmol). After stirring for 30 minutes, partial evaporation of the solvent and addition of cold methanol or diethyl ether (10 ml) afforded yellow solids, which were filtered off, washed with water and dried *in vacuo*.

***12**.* Yield 97%. mp 184 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C) δ 3.00 (s, 4 H, SCH_2CH_2S) and 1.01–0.62 (m, 6 H, CH_3). IR (cm^{-1}) 1065, 1040 (C=S) and 515, 464 (Sn–Me). Elemental anal. Calc. for $C_{10}H_{10}SnS_{10}$: C, 21.1; H, 1.8; S, 56.3%. Found: C, 20.7; H, 1.9; S, 55.4%.

13. Yield 14%. mp 200 °C. ^1H NMR (300 MHz, [D$_6$]DMSO, 25 °C) δ 7.29–7.27 (m, 4 H, Ph), 4.56–4.24 (m, 4 H, SCH_2), 1.23 (s, 3 H, CH_3) and 1.0 (s, 3 H, CH_3). IR (cm^{-1}) 1066, 1030 (C=S) and 575, 455 (Sn–Me). Elemental anal. Calc. for $C_{16}H_{14}S_{10}Sn$: C, 37.2; H, 2.7; S, 24.8%. Found: C, 37.5; H, 2.9; S, 24.7%.

14. Yield 85%. mp 92 °C. ^1H NMR (300 MHz, [D$_6$]DMSO, 25 °C) δ 7.29–7.16 (m, 4 H, Ph), 4.12 (s, 4 H, SCH_2) and 0.9 (s, 6 H, J (Sn–H) = 114 Hz, CH_3). IR (cm^{-1}) 1128 (br) (C=S) and 517, 441 (Sn–Me). Elemental anal. Calc. for $C_{16}H_{14}SnS_{10}$: C, 29.8; H, 2.2; S, 49.6 %. Found: C, 30.3; H, 2.5; S, 48.2%.

15. Yield 85%. mp 172 °C. ^1H NMR (300 MHz, [D$_6$]DMSO, 25 °C) δ 7.23 (s, 4 H, Ph), 4.10 (s, 4 H, SCH_2), 0.67–1.0 (m, 6 H, CH_3). IR (cm^{-1}) 1058, 1020 (C=S) and 516, 465 (Sn–Me). Elemental anal. Calc. for $C_{16}H_{14}SnS_{10}$: 29.8; H, 2.2; S, 49.6 %. Found: C, 30.2; H, 2.3; S, 48.5%.

16. Yield 75%. mp 132 °C. ^1H NMR (300 MHz, [D$_6$]DMSO, 25 °C) δ 7.65 (t, 1 H, J (H,H) = 13 Hz), 7.20 (d, 2 H, J (H,H) = 13 Hz), 4.25 (s, 4 H, SCH_2) and 1.30–0.60 (m, 6 H, CH_3). IR (cm^{-1}) 1060, 1020 (C=S) and 573, 465 (Sn–Me). Elemental anal. Calc. for $C_{15}H_{13}NSnS_{10}$ C, 27.4; H, 2.2; N, 1.8; S, 48.3%. Found: C, 27.9; H, 2.1; N, 2.2; S, 49.6%.

General procedure for the synthesis of gold derivatives 17–21 [Au$_2$(dmit–bridge–dmit)(PPh$_2$Me)$_2$]. *Method (a).* To a suspension of the corresponding protected dithiolate **6**–**10** (0.1 mmol) in ethanol (10 ml) was added a solution of NaOEt (4 ml, 0.1 M, 0.4 mmol;) with stirring and cooling using an ice-bath, followed by [AuCl(PPh$_2$Me)] (0.0864 g, 0.2 mmol). After stirring for 6 hours, the yellow solids obtained were filtered off, washed with ethanol and dried *in vacuo*.

Method (b). To a suspension of the corresponding tin derivative **12**–**16** (0.1 mmol) in ethanol (10 ml), cooled by an ice-bath, was added [AuCl(PPh$_2$Me)] (0.0864 g, 0.2 mmol). After stirring overnight, the yellow solids obtained were filtered off, washed with ethanol and dried *in vacuo*.

17. Yield (a) 95%, (b) 72%. mp 87 °C. MS (LSIMS$^+$): *m*/*z* (%): 1215 (5, M$^+$), 1223 (20, [S(AuPPh$_2$Me)$_3$]$^+$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.65–7.59 (m, 8 H, Ph), 7.57–7.49 (m, 12 H, Ph), 2.99 (s, 4 H, SCH_2CH_2S) and 2.14 (d, 6 H, J (P–H) = 10 Hz, CH_3). ^{31}P-{^1H}NMR (300 MHz, $CDCl_3$, 25 °C): δ 22.1 (s). IR (cm^{-1}) 1058, 1020 (C=S). Elemental anal. Calc. for $C_{34}H_{30}Au_2P_2S_{10}$ C, 33.6; H, 2.5; S, 26.4%. Found: C, 33.7; H, 2.5; S, 26.1%.

18. Yield 98%, method (a). mp 95 °C. MS (LSIMS$^+$): *m*/*z* (%): 1292 (3, M$^+$), 1223 (10, [S(AuPPh$_2$Me)$_3$]$^+$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.63–7.56 (m, 8 H, P*Ph*$_2$Me), 7.46–7.30 (m, 12 H, P*Ph*$_2$Me), 7.16–7.11 (m, 2H), 7.10–7.08 (m, 2 H), 4.20 (s, 4 H, SCH_2) and 2.07 (d, 6 H, J (P–H) = 10 Hz, CH_3). ^{31}P-{^1H}NMR (300 MHz, $CDCl_3$, 25 °C): δ 21.9 (s). IR (cm^{-1}) 1057, 1020 (C=S). Elemental anal. Calc. for $C_{40}H_{34}Au_2P_2S_{10}$ C, 37.2; H, 2.7; S, 24.8%. Found: C, 37.5; H, 2.8; S, 24.4%.

19. Yield 98%, method (a). mp 82 °C. MS (LSIMS$^+$): *m*/*z* (%): 1223 (32, [S(AuPPh$_2$Me)$_3$]$^+$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.68–7.61 (m, 8 H, P*Ph*$_2$Me), 7.53–7.42 (m, 12 H, P*Ph*$_2$Me), 7.26–7.22 (m, 2 H), 7.22–7.13 (m, 2 H), 4.13–3.9 (s, 4 H, SCH_2) and 2.12 (d, 6 H, J (P–H) = 10 Hz, CH_3). ^{31}P-{^1H}NMR (300 MHz, $CDCl_3$, 25 °C): δ 21.7 (s). IR (cm^{-1}) 1058, 1022 (C=S). Elemental anal. Calc. for $C_{40}H_{34}Au_2P_2S_{10}$ C, 37.2; H, 2.7; S, 24.8%. Found: C, 37.1; H, 2.7; S, 25.1%.

20. Yield (a) 98%, (b) 50%. mp 95 °C. MS (LSIMS$^+$): *m*/*z* (%): 1223 (44, [S(AuPPh$_2$Me)$_3$]$^+$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.64–7.57 (m, 8 H, P*Ph*$_2$Me), 7.49–7.48 (m, 12 H, P*Ph*$_2$Me), 7.25–7.12 (m, 2 H), 7.01 (s, 2 H), 3.90 (s, 4 H, SCH_2) and 2.08 (d, 6 H, J 10 Hz, CH_3). ^{31}P-{^1H}NMR (300 MHz, $CDCl_3$, 25 °C): δ 22.1 (s). IR (cm^{-1}) 1055, 1022 (C=S). Elemental anal. Calc. for $C_{40}H_{34}Au_2P_2S_{10}$ C, 37.2; H, 2.7; S, 24.8%. Found: C, 37.3; H, 2.8; S, 24.6%.

21. Yield (a) 98%, (b) 55%. mp 80 °C. MS (LSIMS$^+$): *m*/*z* (%): 1223 (74, [S(AuPPh$_2$Me)$_3$]$^+$); 1292 (4, M$^+$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.65–7.55 (m, 8 H, P*Ph*$_2$Me), 7.52–7.45 (m, 12 H, P*Ph*$_2$Me), 7.44 (t, 1 H, J (H–H) = 7 Hz), 7.02 (d, 2 H, J (H–H) = 7 Hz), 3.97 (s, 4 H, SCH_2) and 2.12 (d, 6 H, J (P–H) = 10 Hz, CH_3). ^{31}P-{^1H}NMR (300 MHz, $CDCl_3$, 25 °C): δ 22.0 (s). IR (cm^{-1}) 1059, 1023 (C=S). Elemental anal. Calc. for $C_{39}H_{33}NAu_2P_2S_{10}$ C, 36.3; H, 2.6; N, 1.1; S, 24.8%. Found: C, 36.5; H, 2.7; N, 1.2; S, 24.5%.

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