Metal complexes of a tetrathiafulvalene 4,5-dithiolate. Synthesis, characterisation and properties of dianionic and neutral mercury complexes

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Dianionic mercury bis(tetrathiafulvalene dithiolate) complexes $[NMe_4]_2[Hg(R_2C_6S_8)_2]$ (R = Et or Bu) and the corresponding oxidised neutral complex $[Hg(R_2C_6S_8)_2]$ (R = Et) have been prepared. The crystal structure of $[NMe_4]_2[Hg(R_2C_6S_8)_2]$ (R = Et) has been determined and shows that the tetrathiafulvalene dithiolate units are tetrahedrally co-ordinated around the central Hg atom. Cyclic voltammetry and ESR studies indicated that there is very little interaction between the two ligands. A compressed pellet of the powdered neutral complex exhibited an electrical conductivity of 10^{-5} S cm^{-1} at room temperature.

Metal complexes of sulfur ligands have been of great interest for many years because of their applications in analytical chemistry, catalysis and their relevance to bioinorganic systems.[1-4] More recent developments have been concerned with the unusual solid-state properties that are found for some of these compounds. Currently, there is much interest in the search for new and improved synthetic molecular metals and in this context organic π-donors based on tetrathiafulvalene [2-(1,3-dithiol-2-ylidene)-1,3-dithiole] (ttf) derivatives and their cation radical salts have been the subject of numerous studies due to their ability to form molecular metals and superconductors at low temperature.[5] Extensive studies on the metal complexes of 4,5-disulfanyl-1,3-dithiole-2-thionate $(C_3S_5^{2-})$ have also been carried out in recent years and salts of the form $A[M(C_3S_5)_2]_2$ where A is a Group 1 metal cation, a closed-shell organic cation such as NMe_4^+, or an open-shell organic cation such as ttf$^+$ often exhibit metallic/conducting properties.[6] For example $[ttf][Ni(C_3S_5)_2]_2$ 1 behaves as a superconductor $[(T_c = 1.62$ K at 7 kbar) $(7 \times 10^8$ Pa)].[7]

We and others have recently developed routes to tetrathiafulvalene dithiolates I which serve as excellent precursors for a variety of unsymmetrical ttf derivatives.[8,9] We reasoned that these dithiolates could be used as ligands for metal complexes which contain the ttf moiety, which could also be regarded as extended C_3S_5 systems (Scheme 1). Metal complexes 2 of these ligands would therefore have an increased potential for intramolecular stacking and orbital overlap which could lead to enhanced conduction properties. Additionally, the presence of three potentially redox-active centres within the same molecule (i.e. the MS_4 core and the two ttf fragments of the ligands) could give rise to new multistate properties in this class of compound.

We have found one previous report of a neutral bis(tetrathiafulvalene dithiolate) complex of Ni which was reported to be an insulator.[10] Polymeric metal complexes of tetrathiafulvalene tetrathiolate have also been described.[11] In the present paper we report the synthesis and for the first time the complete characterisation of a dianionic, metal bis(ttf dithiolate) (including a crystal structure) and the corresponding neutral complex prepared by oxidation.

Results and Discussion

Synthesis of the dianionic species

We chose to prepare the tetrathiafulvalene dithiolates, to be used in the preparation of metal complexes, from bis(2-
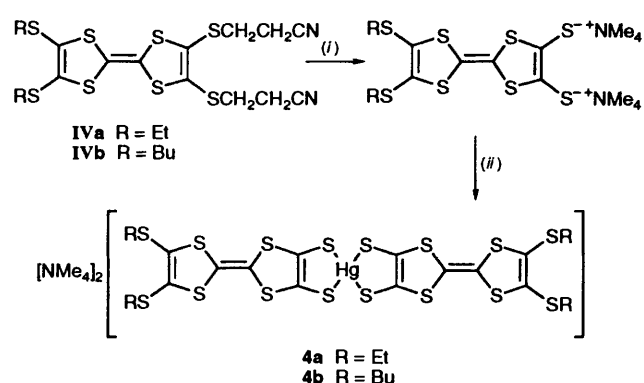

1 M = Ni, A = ttf$^+$

I

2

Scheme 1
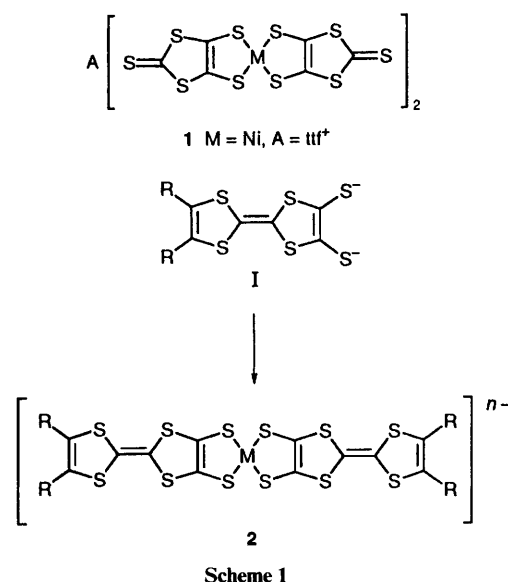
cyanoethylsulfanyl)tetrathiafulvalenes following the method of Becher et al.[9] The reaction of 4,5-bis(2-cyanoethylsulfanyl)-1,3-dithiol-2-one III and 4,5-bis(alkylsulfanyl)-1,3-dithiole-2-thione IIa or IIb (prepared by alkylation of the readily available zinc complex 3[12]) in neat triethyl phosphite at 100 °C afforded the ttf derivative IVa or IVb in 53 and 51% yield respectively (Scheme 2). Initial attempts at preparing tetrathiafulvalene dithiolate metal complexes involved deprotection of compounds IVa and IVb with CsOH in dichloromethane as described in the literature,[9b] followed by addition of tetraethylammonium bromide and then $Hg(O_2CMe)_2$ as described for the synthesis of $[NEt_4]_2[M(C_3S_5)_2]_2$ salts.[6b] The resulting product appeared to be the desired metal complexes but contaminated with a mixture of tetraethylammonium and caesium counter cations (as evidenced by NMR spectra of the complexes). In order to avoid this problem we switched to using tetramethylammonium hydroxide as the base to generate the dithiolate. With dichloromethane as solvent, however, poor yields of the dithiolate were obtained since it appeared to react with the solvent. Indeed deprotection of IVb with NMe_4OH in dichloromethane, followed by addition of an excess of methyl iodide after 20 min, led to the bis(tetrathiafulvalene) V derivative in 41% isolated yield,[13] along with other higher oligomers (Scheme 3).

Table 1 Selected bond distances (Å) and angles (°) for complex **4a**

Hg–S(1)	2.565(4)	Hg–S(9)	2.518(4)	S(7)–C(5)	1.74(2)	S(14)–C(16)	1.78(2)
Hg–S(2)	2.517(4)	Hg–S(10)	2.522(4)	S(7)–C(7)	1.86(2)	S(15)–C(15)	1.73(2)
S(1)–C(1)	1.71(2)	S(9)–C(11)	1.74(1)	S(8)–C(6)	1.76(2)	S(15)–C(17)	1.89(2)
S(2)–C(2)	1.73(2)	S(10)–C(12)	1.75(2)	S(8)–C(9)	1.83(2)	S(16)–C(16)	1.75(2)
S(3)–C(1)	1.77(1)	S(11)–C(11)	1.75(1)	C(1)–C(2)	1.36(2)	S(16)–C(19)	1.95(3)
S(3)–C(3)	1.75(2)	S(11)–C(13)	1.76(1)	C(3)–C(4)	1.35(2)	C(11)–C(12)	1.36(2)
S(4)–C(2)	1.81(1)	S(12)–C(12)	1.77(1)	C(5)–C(6)	1.34(2)	C(13)–C(14)	1.40(2)
S(4)–C(3)	1.75(2)	S(12)–C(13)	1.74(2)	C(7)–C(8)	1.54(2)	C(15)–C(16)	1.33(2)
S(5)–C(4)	1.76(2)	S(13)–C(14)	1.72(2)	C(9)–C(10)	1.44(3)	C(17)–C(18)	1.45(3)
S(5)–C(5)	1.76(2)	S(13)–C(15)	1.79(2)	S(6)···S(8a)	3.96	C(19)–C(20)	1.38(3)
S(6)–C(4)	1.73(2)	S(14)–C(14)	1.75(1)	S(8)···S(16c)	4.00	S(8)···S(15b)	3.96
S(6)–C(6)	1.77(2)						
S(1)–Hg–S(2)	87.6(1)	S(2)–Hg–S(9)	126.9(2)	C(4)–S(5)–C(5)	94.0(8)	C(14)–S(13)–C(15)	94.8(7)
S(1)–Hg–S(9)	112.8(2)	S(2)–Hg–S(10)	120.8(1)	C(4)–S(6)–C(6)	93.8(7)	C(14)–S(14)–C(16)	93.6(7)
S(1)–Hg–S(10)	123.1(1)	S(9)–Hg–S(10)	89.3(1)	C(5)–S(7)–C(7)	101.2(7)	C(15)–S(15)–C(17)	101.4(9)
Hg–S(1)–C(1)	97.5(5)	Hg–S(9)–C(11)	96.9(5)	C(6)–S(8)–C(9)	106.9(9)	C(16)–S(16)–C(19)	98.0(9)
Hg–S(2)–C(2)	96.7(5)	Hg–S(10)–C(12)	96.1(5)	S(7)–C(7)–C(8)	111(1)	S(15)–C(17)–C(18)	112(2)
C(1)–S(3)–C(3)	95.4(7)	C(11)–S(11)–C(13)	94.7(7)	S(8)–C(9)–C(10)	110(2)	S(16)–C(19)–C(20)	112(2)
C(2)–S(4)–C(3)	93.7(7)	C(12)–S(12)–C(13)	95.0(7)				

Symmetry operations: a 1 − x, 1 − y, 2 − z; b x − 1, y + 1, z + 1; c x − 1, y + 1, z.
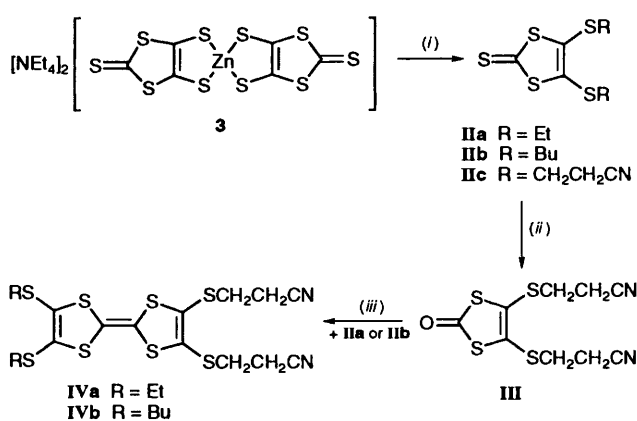
Scheme 2 (i) RBr, MeCN, reflux; (ii) Hg(O₂CMe)₂, CH₂Cl₂–MeCO₂H, 50 °C; (iii) P(OEt)₃, 100 °C

IIa R = Et
IIb R = Bu
IIc R = CH₂CH₂CN

IVa R = Et
IVb R = Bu

III
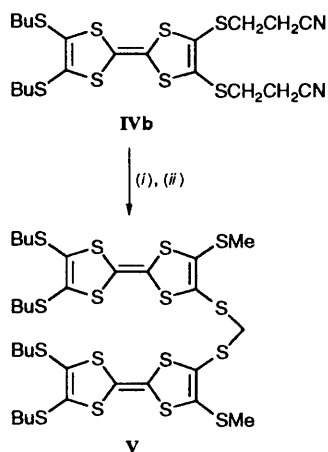
Scheme 3 (i) 2.2 equivalents NMe₄OH, CH₂Cl₂; (ii) MeI, tetrahydrofuran (thf)

IVb

V

Scheme 4 (i) 2.2 equivalents NMe₄OH, thf; (ii) Hg(O₂CMe)₂, MeOH

IVa R = Et
IVb R = Bu

4a R = Et
4b R = Bu

Deprotection of compound **IVa** or **IVb** with 2 equivalents of NMe₄OH in thf, however, cleanly gave the tetramethylammonium tetrathiafulvalene dithiolate salts as red precipitates. After removal of the thf *in vacuo*, the salts were dissolved in MeOH and treated with 0.5 equivalent of Hg(O₂CMe)₂, resulting in precipitation of the dianionic metal complexes **4a** and **4b** (Scheme 4). The complexes were washed with MeOH, dissolved

in acetone and precipitated with diethyl ether, to give analytically pure samples in over 90% yield.

Crystal structure

Beautiful orange, plate-shaped crystals of complex **4a** were grown by slow diffusion of diethyl ether into an acetone solution of it. The structure consists of discrete anions (see Fig. 1 and Table 1) and tetramethylammonium cations. The structure solution emerged in a straightforward manner with no evidence for disorder in terms of atom sites, but the poor geometry around N(2) in one of the cations suggested disorder and this was modelled using restraints in the least-squares refinement. The large isotropic thermal parameters for the eight ethyl group C atoms and the C–C bond lengths associated with some of the ethyl groups also indicated some disorder in these peripheral groups.

The mercury atom is approximately tetrahedrally co-ordinated with Hg–S distances 2.517(4)–2.565(4) Å and as expected the S–Hg–S angles within the five-membered rings are smaller [88.4° (average)] than the idealised tetrahedral value. The two planes S(1)–Hg–S(2) and S(9)–Hg–S(10) are approximately perpendicular to each other. The S–C distances within the ttf residue [1.71(2)–1.81(1) Å] are shorter than the S–C of the terminal ethyl groups [1.83(2)–1.95(3) Å] and the formal C=C distances are in accord with the multiple bond.

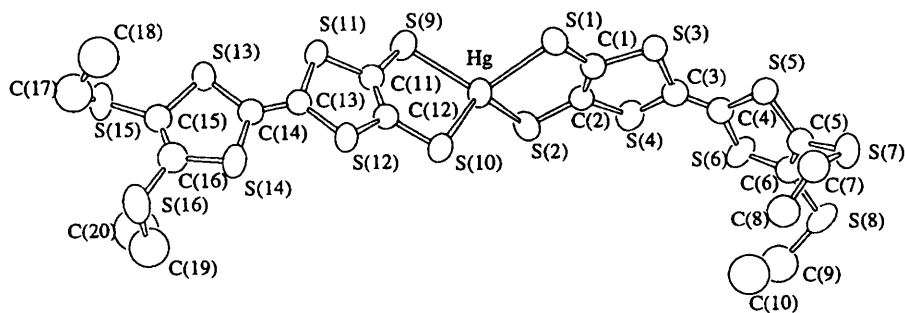A tetrahedral geometry around Hg is also found in

Fig. 1 An ORTEP representation[14] of the dianion $[Hg(C_{10}H_{10}S_8)_2]^{2-}$ **4a** showing the atom labelling and with atom surfaces drawn at the 50% probability level
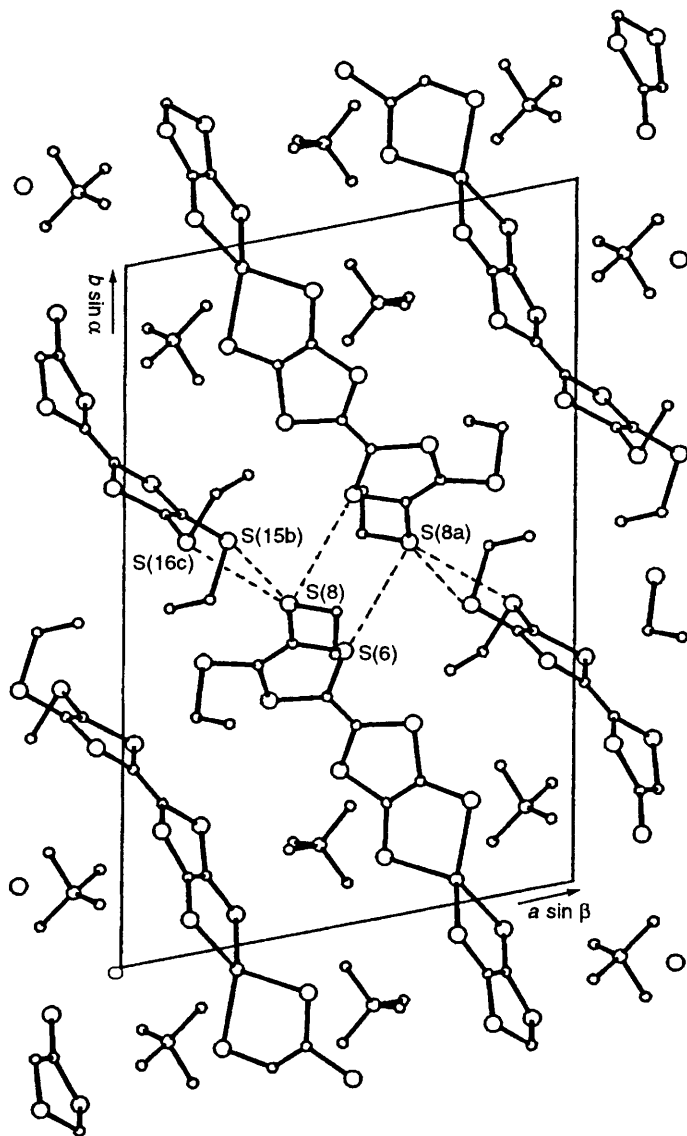

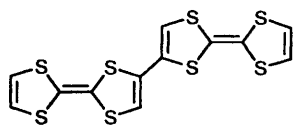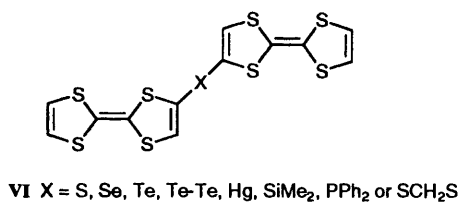**Fig. 2** Packing diagram for complex **4a** showing the arrangement of the anions and the short intermolecular S · · · S contacts

metacinnabarite, HgS (Hg–S 2.54 Å) however closer to the present compound is $(C_{10}H_{12}S_8)(HgI_2)_2$.[15] The ttf geometry (C=C and C–S) agrees with the present study but the co-ordination from the MeS residues gives, as might be expected, a longer Hg–S distance [3.1 Å (average)].

The two ttf units in the anion are non-planar with one exhibiting a deviation from planarity of 37.9° and the other 50.7°. The angle of deviation was taken as the angle between the plane defined by four atoms S(3), C(1), C(2), S(4) and that defined by S(5), C(5), C(6), S(6) and correspondingly for the other ttf unit. These deviations are probably due to packing

effects caused by adjacent ttf units lying orthogonal to each other and establishing short intermolecular S · · · S distances contacts (see Fig. 2 and Table 1).

Electrochemical studies

Cyclic voltammetry (CV) of complex **4a** was carried out on a macroscopic platinum-disc electrode in dichloromethane, using $NBu^n_4BF_4$ as supporting electrolyte, between -0.6 and $+1.5$ V at 50 mV s^{-1}. Four oxidation processes were seen with midpoint potentials at -0.04, $+0.07$, $+0.76$ and $+1.09$ V vs. the saturated calomel electrode (SCE) and peak heights of $1:1:2:1$

VI X = S, Se, Te, Te-Te, Hg, SiMe$_2$, PPh$_2$ or SCH$_2$S

VII

Scheme 5

[NMe$_4$]$_2$

4a

(i)

5

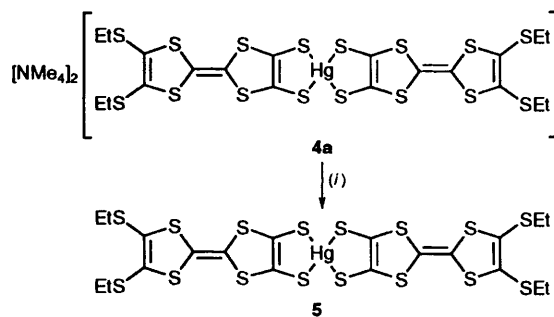**Scheme 6** (i) 0.5 equivalent I$_2$, MeCN, room temperature

respectively. Use of chronoamperometry combined with CV at a microelectrode[16] showed that the peaks at -0.04 and $+0.07$ V were due to two one-electron oxidations [$D = (5.6 \pm 0.5) \times 10^{-6}$ cm^2 s^{-1}]. The third wave is presumably due to the second oxidation of each of the two ttf moieties within the complex which is consistent with the relative peak heights, but detailed analysis of the third and fourth waves is complicated by deposition of the first oxidation product as a light brown film on the electrode surface. Cyclic voltammetry in acetonitrile differed from that in dichloromethane in that the first two peaks coalesce to give a single peak at -0.54 V vs. Ag-Ag$^+$ with the other two processes occurring irreversibly at $+0.45$ and $+0.5$ V.* The single two-electron oxidation observed in MeCN and the small separation between the first two one-electron oxidation potentials in dichloromethane indicate that oxidation of the first ttf does not significantly affect the ease with which the second ttf is oxidised. The almost complete absence of interaction between the two ttf units as indicated by these CV studies is confirmed by ESR studies on the oxidised neutral complex **5** (see below). This is not surprising in view of observations reported for a range of ttf–X–ttf dimers **VI** (X = S, Se, Te, Te–Te, Hg, SiMe$_2$, PPh$_2$, or SCH$_2$S)[13,17,19] and for **VII** (where the two redox groups are directly linked)[20] (Scheme 5). The small separations between the first two oxidation waves for these compounds is similarly attributed to the lack of interaction between the two ttf units, and this has been supported by extended-Hückel calculations.[19]

Synthesis and physical properties of the neutral species

The addition of a stoichiometric amount of I$_2$ to a solution of complex **4a** in acetonitrile at room temperature resulted in the rapid formation of a brown precipitate. After filtration and washing with MeCN and MeOH the neutral complex **5** was isolated analytically pure in 80% yield (Scheme 6). In view of the small separation of the first two oxidation potentials, as determined by CV, it is not surprising that all attempts to oxidise **4a** chemically to the corresponding monoanionic species failed, always resulting in a mixture of the neutral and the dianionic species.

The ESR spectrum of complex **5** was measured in the solid state at room temperature and contained a singlet with a g value of 2.0052 which is consistent with radicals localised on the two ttf units. The dianionic complex would be expected to be diamagnetic and oxidation to the neutral complex removes two electrons. Since **5** is expected to have tetrahedral co-ordination about the Hg atom (as observed for **4a**) there will be little interaction between the π systems on the two ligands. Thus, each ttf-based ligand contains an essentially independent single electron, which accounts for the singlet observed in the ESR spectrum of the neutral compound and the small separation between the first two oxidation waves in the CV studies carried out on the dianion.

Compressed pellets of powdered complex **5** consistently exhibited an electrical conductivity of 10^{-5} S cm^{-1} at room temperature. This compares with $< 10^{-7}$ S cm^{-1} at room temperature for the dianion salt **4a**. The conductivity for the neutral compound **5**, while not especially high compared to those of many charge-transfer salts, is nevertheless noteworthy for what is, from the analysis, an undoped molecular solid.[21] This is especially so since the co-ordination to the mercury cation in the neutral complex is expected to be tetrahedral as found for the dianionic compound, and therefore a columnar stacked structure is not feasible. Higher conductivities may therefore be observed for a complex in which the co-ordination about the central metal atom is square planar. Further studies directed at the preparation of the complexes of Ni and Pd are currently underway.

Experimental

Syntheses

4,5-Bis(2-ethylsulfanyl)-1,3-dithiole-2-thione IIa. Following the procedure of Becher et al.,[9] reaction of the zinc complex **3** with ethyl bromide in MeCN gave compound **IIa** as an orange oil in 76% yield: δ_H(CDCl$_3$, SiMe$_4$) 2.88 (4 H, q) and 1.33 (6 H, t); δ_C(CDCl$_3$, SiMe$_4$) 211.46, 136.50, 31.19 and 15.18.

4,5-Bis(2-butylsulfanyl)-1,3-dithiole-2-thione IIb. Following the procedure of Becher et al.,[9] reaction of the zinc complex **3** with butyl bromide in MeCN gave compound **IIb** as an orange

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* Shifts in the position of all peaks of about 0.5 V on going from dichloromethane to acetonitrile are expected due to the change in solvent and reference electrode system. For example the voltammetry of ferrocene–ferrocenium also shifts by between 0.45 and 0.5 V on going from dichloromethane to acetonitrile under the same conditions and with the same respective reference electrodes. The less significant changes in the relative positions of the first and second oxidation waves are presumably due to solvent effects.

oil in 78% yield: δ_H(CDCl$_3$, SiMe$_4$) 2.67 (4 H, q), 1.44 (4 H, m), 1.20 (4 H, m) and 0.68 (6 H, t); δ_C(CDCl$_3$, SiMe$_4$) 210.94, 136.38, 36.65, 31.88, 22.12 and 13.84.

2-[4,5-Bis(ethylsulfanyl)-1,3-dithiol-2-ylidene]-4,5-bis(2-cyanoethylsulfanyl)-1,3-dithiole IVa.

Following the procedure of Becher et al.,[9] coupling of compounds IIa and III in neat P(OEt)$_3$ at reflux gave the bis(protected) compound IVa as an orange solid (53%), m.p. = 84–85 °C: δ_H(CDCl$_3$, SiMe$_4$) 3.02 (4 H, t), 2.80 (4 H, q), 2.69 (4 H, t) and 1.25 (6 H, t); δ_C(CDCl$_3$, SiMe$_4$) 128.15, 128.06, 117.67, 114.87, 106.95, 31.44, 30.76, 19.10 and 15.28.

Table 2 Experimental crystallographic data for complex 4a

Formula	C$_{28}$H$_{44}$HgN$_2$S$_{16}$
M	1122.22
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
$a/\text{Å}$	13.846(3)
$b/\text{Å}$	21.935(8)
$c/\text{Å}$	7.802(3)
$\alpha/°$	98.85(3)
$\beta/°$	95.26(3)
$\gamma/°$	78.22(2)
$U/\text{Å}^3$	2287.6(1.3)
T/K	298
Density (calc.)/g cm^{-3}	1.629
Z	2
$F(000)$	1124
Crystal size/mm	0.50 × 0.15 × 0.05
Scan type	ω–2θ
Total no. of observations	6509
Total no. of unique observations	5158
No. data used in refinement [$F > 3\sigma(F)$]	3399
No. parameters	275
No. restraints	5
Weighting scheme, w^{-1}	$\sigma^2(F_o) + 0.0005F_o^2$
λ(Mo-Kα)/Å	0.710 69
μ/cm^{-1}	40.5
Maximum 2θ/°	50.0
hkl Limits	0–16, −23 to 23, 8 to −8
Maximum |shift/e.s.d.|	0.2
Maximum, minimum residual electron density/e Å^{-3}	1.0, −0.7
R	0.068
R'	0.065

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

2-[4,5-Bis(2-cyanoethylsulfanyl)-1,3-dithiol-2-ylidene]-4,5-bis(butylsulfanyl)-1,3-dithiole IVb.

Following the procedure of Becher et al.,[9] coupling of compounds IIb and III in neat P(OEt)$_3$ at reflux gave the bis(protected) compound IVb as an orange solid (51%), m.p. = 94–95 °C: δ_H(CDCl$_3$, SiMe$_4$) 3.05 (4 H, t), 2.82 (4 H, t), 2.72 (4 H, t), 1.59 (4 H, m), 1.42 (4 H, m) and 0.88 (6 H, t); δ_C(CDCl$_3$, SiMe$_4$) 128.12, 127.97, 117.68, 106.73, 36.19, 31.86, 31.42, 21.77, 19.08 and 13.78.

Bis-ttf derivative V. Tetramethylammonium hydroxide [210 μl of a 25% (w/w) solution in MeOH, 0.506 mmol] was added to compound IVb (125 mg, 0.23 mmol) in dichloromethane at 0 °C. The reaction mixture was stirred for 20 min and the solvents were removed in vacuo. The crude product was then suspended in thf and cooled to 0 °C, followed by the addition of MeI (31 μl, 0.506 mmol). The reaction mixture was stirred at 20 °C overnight, concentrated in vacuo and the resulting product dissolved in dichloromethane and washed with water (2 × 30 cm^3). The organic layer was dried (MgSO$_4$) for 1 h, concentrated in vacuo and the product purified by column chromatography [silica gel; eluent, dichloromethane–light petroleum (b.p. 40–60 °C)(1:5)] to give compound V as an orange oil (43 mg, 41%), R_f = 0.26 [dichloromethane–light petroleum (1:3)]: δ_H(CDCl$_3$, SiMe$_4$) 4.08 (2 H, s), 2.75 (8 H, t), 2.38 (6 H, s), 1.53 (8 H, m), 1.38 (8 H, m) and 0.87 (12 H, t); δ_C(CDCl$_3$, SiMe$_4$) 134.0, 128.1, 127.9, 122.6, 112.1, 42.7, 36.3, 32.0, 21.9, 19.6 and 13.9; mass spectrum (electron impact) m/z 928 (M^+).

Dianionic complex 4a. The compound NMe$_4$OH [2.88 cm^3 of a 25% (w/w) solution in MeOH, 6.84 mmol] was added to IVa (1.36 g, 2.74 mmol) in thf (20 cm^3) at 0 °C under argon and the reaction mixture left stirring at this temperature for 20 min. The thf was then removed in vacuo and the resulting product dissolved in MeOH (10 cm^3). The compound Hg(O$_2$CMe)$_2$ (0.44 g, 1.37 mmol) in MeOH (5 cm^3) was added and the reaction mixture stirred overnight at 20 °C. The resulting precipitate was filtered off, washed with MeOH and Et$_2$O and finally dried in vacuo. Further crystallisation (acetone–Et$_2$O) gave complex 4a as golden crystals (1.43 g, 93%), m.p. = 100–102 °C (Found: C, 30.05; H, 3.60; N, 2.40. C$_{28}$H$_{44}$HgN$_2$S$_{16}$ requires C, 29.95; H, 3.95; N, 2.50%); δ_H(CD$_3$COCD$_3$, SiMe$_4$) 3.35 (24 H, s), 2.87 (8 H, q) and 1.27 (t, 12 H).

Table 3 Atomic coordinates for complex 4a

Atom	x	y	z
Hg	0.743 34(6)	0.034 43(3)	0.503 89(10)
S(1)	0.583 7(3)	0.086 7(2)	0.348 1(6)
S(2)	0.774 0(3)	0.143 1(2)	0.615 7(6)
S(3)	0.482 6(3)	0.221 1(2)	0.393 1(6)
S(4)	0.645 1(3)	0.267 8(2)	0.603 1(6)
S(5)	0.323 7(3)	0.339 5(2)	0.585 5(6)
S(6)	0.490 7(4)	0.389 4(2)	0.771 0(6)
S(7)	0.176 7(4)	0.411 3(2)	0.838 9(7)
S(8)	0.366 5(4)	0.472 5(2)	1.046 9(6)
S(9)	0.848 6(4)	−0.049 4(2)	0.305 6(6)
S(10)	0.747 2(3)	−0.044 5(2)	0.709 2(6)
S(11)	0.912 7(3)	−0.184 4(2)	0.327 4(5)
S(12)	0.826 8(3)	−0.181 3(2)	0.658 4(6)
S(13)	1.058 7(3)	−0.318 8(2)	0.383 6(6)
S(14)	0.974 8(3)	−0.314 3(2)	0.717 9(6)
S(15)	1.228 8(4)	−0.421 2(2)	0.442 8(7)
S(16)	1.137 0(5)	−0.411 7(3)	0.846 4(8)
N(1)	0.438 5(10)	0.122 2(6)	−0.154 9(18)
N(2)	0.894 8(9)	0.119 2(6)	0.116 5(18)
C(1)	0.586 7(11)	0.162 8(7)	0.437 0(20)
C(2)	0.662 1(11)	0.183 9(6)	0.537 3(19)
C(3)	0.518 0(11)	0.280 5(7)	0.548 4(20)
C(4)	0.452 9(11)	0.329 0(7)	0.627 2(20)
C(5)	0.298 0(11)	0.392 5(7)	0.776 4(20)
C(6)	0.374 8(11)	0.414 4(7)	0.862 8(20)
C(7)	0.161 9(14)	0.335 3(8)	0.902 6(24)
C(8)	0.235 3(14)	0.317 0(9)	1.055 8(25)
C(9)	0.472 1(17)	0.448 2(11)	1.197 4(30)
C(10)	0.470 4(18)	0.386 9(12)	1.239 8(33)
C(11)	0.853 7(11)	−0.110 7(6)	0.425 9(19)
C(12)	0.814 4(11)	−0.108 5(6)	0.580 1(19)
C(13)	0.911 6(11)	−0.222 3(6)	0.510 1(19)
C(14)	0.976 6(11)	−0.278 5(7)	0.533 5(19)
C(15)	1.126 1(11)	−0.370 9(7)	0.527 0(21)
C(16)	1.089 7(13)	−0.366 3(8)	0.681 0(23)
C(17)	1.190 0(17)	−0.499 9(11)	0.424 0(31)
C(18)	1.101 2(19)	−0.502 0(11)	0.310 3(34)
C(19)	1.202 3(19)	−0.350 3(11)	0.995 6(33)
C(20)	1.272 9(22)	−0.332 4(13)	0.910 5(39)
C(21)	0.371 1(16)	0.123 3(10)	−0.004 4(28)
C(22)	0.505 8(19)	0.168 0(12)	−0.100 5(34)
C(23)	0.500 9(22)	0.059 4(13)	−0.175 1(38)
C(24)	0.380 1(19)	0.133 0(11)	−0.320 5(35)
C(25)	0.951 3(12)	0.095 5(8)	0.270 4(23)
C(26)	0.952 0(21)	0.145 3(13)	0.004 1(37)
C(27)	0.824 3(25)	0.078 2(12)	0.044 1(41)
C(28)	0.836 5(30)	0.183 3(12)	0.172 0(45)

Dianionic complex 4b. Following the above procedure, compound **IVb** (1.33 g, 2.42 mmol), NMe$_4$OH [2.24 cm^3 of a 25% (w/w) solution in MeOH, 5.32 mmol] and Hg(O$_2$CMe)$_2$ (385 mg, 1.21 mmol) gave the dianionic complex **4b** as an orange powder (1.43 g, 96%), m.p. = 149–152 °C (Found: C, 34.90; H, 4.75; N, 2.55. C$_{36}$H$_{60}$HgN$_2$S$_{16}$ requires C, 35.00; H, 4.90; N, 2.25%); δ_H(CDCl$_3$, SiMe$_4$) 3.21 (s, 24 H), 2.84 (8 H, t), 1.63 (8 H, m), 1.46 (8 H, m) and 0.83 (12 H, t).

Neutral complex 5. The dianionic complex **4a** (300 mg, 0.27 mmol) was dissolved in MeCN (100 cm^3) under argon. Iodine (68 mg, 0.27 mmol) was added and the reaction mixture was left stirring overnight at 20 °C. The resulting brown precipitate was filtered off, washed with MeOH (3 × 20 cm^3), with Et$_2$O (3 × 20 cm^3) and finally dried *in vacuo* to give the neutral complex **5** as a brown solid (210 mg, 80%), m.p. = 109–111 °C (Found: C, 24.65; H, 1.75; N, 0.10. C$_{20}$H$_{20}$HgS$_{16}$ requires C, 24.65; H, 2.00; N, 0.00%).

Crystal structure of [NMe$_4$]$_2$[Hg(C$_{10}$H$_{10}$S$_8$)$_2$] 4a

Air-stable orange plates of complex **4a** were grown by slow diffusion of diethyl ether vapour into a solution of it in acetone. Crystallographic data were collected at room temperature from a crystal mounted on a Rigaku AFC7S diffractometer equipped with Mo-Kα radiation and graphite monochromator. In addition to the usual Lorentz and polarisation corrections, a ψ-scan empirical absorption was applied (three reflections; minimum, maximum transmission 0.79, 1.00). The structure was solved using SHELXS 86[22] and refined on F by full-matrix least squares minimising $\Sigma w \Delta^2$ using SHELX 76.[23] 6509 Observed reflections; the final R, R' values were 0.068 and 0.065 for 275 parameters (see Tables 2 and 3). Anisotropic (Hg, S) and isotropic (N, C) atoms were used and no hydrogen atoms were included in the model. There was some disorder associated with one of the cations [N(2)]. Complex neutral-atom scattering factors were taken from SHELX 76 and ref. 24 (Hg).

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Acknowledgements

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