The Preparation and X-Ray Crystal Structure of the First Metal–1,3,2,4-Dithiadiazolylium Salt, $[\mathrm{Hg}(\overline{\mathrm{CNSNS}})_2][\mathrm{AsF}_6]_2$, a Transfer Agent for the Dithiadiazolylium Ring

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The reaction of two equivalents of $[\mathrm{SNS}][\mathrm{AsF}_6]$ with $\mathrm{Hg(CN)_2}$ yields $[\mathrm{Hg}(\overline{\mathrm{CNSNS}})_2][\mathrm{AsF}_6]_2$ **1**, the first example of a dithiadiazolylium ring bonded to a metal centre *via* the carbon; the reaction of **1** with iodine and bromine gave the hexafluoroarsenates(v) of $[\mathrm{I}\text{–}\overline{\mathrm{CNSNS}}]^+$ and previously unreported $[\mathrm{Br}\text{–}\overline{\mathrm{CNSNS}}]^+$, thereby demonstrating the potential of **1** as a transfer reagent for the dithiadiazolylium cation.

Dithionitronium hexafluoroarsenate(v), $[\mathrm{SNS}][\mathrm{AsF}_6]$, is a highly versatile reagent in heterocyclic synthesis. It undergoes cycloaddition reactions, usually in high yield, with C≡C,[1] C≡N,[1,2] C=C,[3] C≡P,[4] C=N,[5a] S≡N,[1a] P=N,[5a] P=P,[5b] and N=N[5a] bonds. The convenient preparations of dithiadiazolylium[2] and dithiazolylium[3] salts have been of particular interest [eqn. (1)].

$$\mathrm{R\text{–}C{\equiv}E} + [\mathrm{SNS}][\mathrm{AsF}_6] \rightarrow [\mathrm{R}\overline{\mathrm{CSNSE}}][\mathrm{AsF}_6] \quad (\mathrm{E = N\ or\ C\text{–}R'}) \tag{1}$$

The rate of cycloaddition of $[\mathrm{SNS}]^+$ has been shown[1b] to be dependent upon the ionisation energy of the dienophile and this explains the increased reactivity of C≡C relative to C≡N. For instance, H–C≡C–C≡N reacts readily with one equivalent of $[\mathrm{SNS}][\mathrm{AsF}_6]$ to give only $[\mathrm{H}\text{–}\overline{\mathrm{CSNSC}}\text{–C≡N}][\mathrm{AsF}_6]$ and no $[\mathrm{H\text{–}C{\equiv}C}\text{–}\overline{\mathrm{CNSNS}}][\mathrm{AsF}_6]$. (Heating to 50 °C for ten weeks is required to complete a second addition[1b] and give $[\mathrm{H}\text{–}\overline{\mathrm{CSNSC}}\text{–}\overline{\mathrm{CNSNS}}][\mathrm{AsF}_6]$.)

We have therefore sought alternative methods of introducing the dithiadiazolylium group, $(\text{–}\mathrm{CN_2S_2}^+)$, which are not dependent on the presence and reactivity of the C≡N group. This could be possible by the reaction of a suitable metal or metalloid dithiadiazolylium derivative $\{\mathrm{M}(\overline{\mathrm{CNSNS}})_x][\mathrm{AsF}_6]_y\}$ with a halide, X–Y, *e.g.*, eqn. (2) for the simple case, M = Hg, $x = y = 2$ and X = Y = I.

$$2\,\mathrm{I_2} + [\mathrm{Hg}(\overline{\mathrm{CNSNS}})_2][\mathrm{AsF}_6]_2 \rightarrow 2[\mathrm{I}\text{–}\overline{\mathrm{CNSNS}}][\mathrm{AsF}_6] + \mathrm{HgI_2} \tag{2}$$

We now report the synthesis and X-ray structural determination of mercury bis-(1,3,2,4-dithiadiazolylium) hexafluoroarsenate(v) **1** and examine its behaviour as (*i*) a typical 1,3,2,4-dithiadiazolylium salt (*e.g.* in metathesis with other counterions and as a cationic initiator for the polymerisation of thf, tetrahydrofuran) and (*ii*) a transfer reagent for the dithiadiazolylium ring, as in eqn. (2).

Pure samples of **1** were prepared by the addition of two equivalents of $[\mathrm{SNS}][\mathrm{AsF}_6]$ to $\mathrm{Hg(CN)_2}$.†

Structurally, compound **1**‡ is equivalent to the known compound $[\overline{\mathrm{SNSNC}}\text{–}\overline{\mathrm{CNSNS}}][\mathrm{AsF}_6]_2$ **2**[1b] but with mercury inserted into the C–C bond. All the corresponding ring distances and angles in **1** and **2** are the same (within experimental error). The Hg–C distance [2.074(12) Å] is longer than in crystalline $\mathrm{Hg(CN)_2}$ [2.019(3) Å[9]]. This is to be expected as a result of the difference in hybridisation of the carbon atoms attached to mercury, *viz* sp in the latter and sp^2 in the dithiadiazolylium cation; analogously the C–C distance is longer in $[\overline{\mathrm{SNSNC}}\text{–}\overline{\mathrm{CNSNS}}]^{2+}$ [1.454(15) Å[1b]] than that in NC–CN [1.37(2) Å[10]]. As in compound **2**, the entire dication is centrosymmetric and essentially planar (Fig. 1).

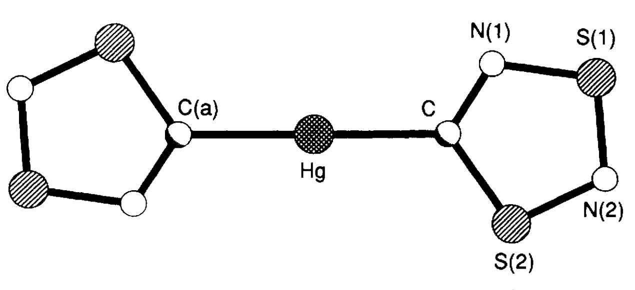

Fig. 1 Structure of the cation of **1**. Selected distances (Å) and angles (°): Hg–C 2.074(12), C–N(1) 1.29(2), N(1)–S(1) 1.622(11), S(1)–N(2) 1.590(10), N(2)–S(2) 1.617(12), S(2)–C 1.734(11), C–Hg–C(a) 180.

The two structures differ considerably in their cation–anion interactions. In **2**, the weak cation–anion interactions are with sulfur (F···S). In the mercury compound **1**, the fluorine atoms of the anion interact with the electropositive metal [at 2.814(9) and 2.916(11) Å]. This gives rise to an approximately octahedral coordination at mercury, as found in $\mathrm{Hg(CN)_2[Se(CH_2)_3]_4}$.[11]

For each anion, two Hg···F interactions are formed with different Hg cations and so the $[\mathrm{AsF}_6]^-$ anion acts as a bridge between cations. As a result, the structure contains polymeric chains of cations and anions (Fig. 2), the chain extending along the crystallographic a axis.

The relative arrangement of the two rings attached to Hg (*i.e.* the *trans*-disposition of the two CN units within the dication) is also found in the solid state structures of other multi-1,3,2,4-dithiadiazolyliums–dithiadiazolyls, *e.g.* $(\overline{\mathrm{CNSNS}}^+)_2$,[1b] $[\mathrm{C}(\overline{\mathrm{CNSNS}})_3]^{2+}$,[2b] and p-$[\overline{\mathrm{SNSNC}}\text{-}\mathrm{C_6H_4}\text{-}\overline{\mathrm{CNSNS}}]$.[2a] Although the cycloaddition mechanism may lead, initially, to the *trans*-geometry of the two rings, the possibility of free rotation about the Hg–C bond (observed at room temperature by NMR and ESR spectroscopy for the C–C bonds in many of these heterocycles[1b]) indicates that the solid-state geometry is dictated by electrostatic and dipole–dipole interactions.

In this case there are no significant secondary interactions involving the ring atoms which would assist the *trans*-arrangement. Another possible explanation[1b,2b] is that the addition of

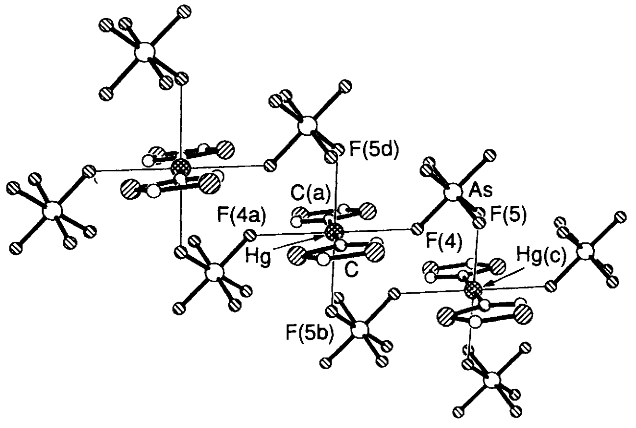

Fig. 2 Part of the polymeric anion-bridged chain structure of **1**. Selected distances (Å) and angles (°): Hg–F(4) 2.814(9), Hg–F(5b) 2.916(11), C–Hg–F(4) 94.8(4), C–Hg–F(5b) 100.0(4), F(4)–Hg–F(5b) 90.7(3) (other details of the Hg coordination follow from the centrosymmetry), Hg–F(4)–As 132.2(5), Hg(c)–F(5)–As 128.3(5).

the second $[\mathrm{SNS}]^+$ unit is facilitated by coordination to the adjacent ring nitrogen (*i.e.* N(1) in $[\mathrm{NC\text{-}Hg}\overline{\mathrm{CN(1)SNS}}]^+$) thus giving a centrosymmetric product.

In order to test dithiadiazolylium transfer properties of **1**, a reaction with I_2 was carried out in liquid sulfur dioxide [see eqn. (2)]. This gave $\mathrm{HgI_2}$ and the known compound $[\mathrm{I\text{-}}\overline{\mathrm{CNSNS}}][\mathrm{AsF_6}]$[1a] as a highly crystalline pale yellow solid (>75% yield, characterised by elemental analysis and IR). The previously unreported salt, $[\mathrm{Br\text{-}}\overline{\mathrm{CNSNS}}][\mathrm{AsF_6}]$, was isolated in 90% yield (characterised by elemental analysis and a comparable IR) from the reaction of **1** with excess of bromine in liquid sulfur dioxide. We are presently examining the chemistry of **1**, particularly its reactivity with other R–X systems.

Anion metathesis of **1**, to give $[\mathrm{Hg}(\overline{\mathrm{CNSNS}})_2][\mathrm{X}]_2$ (X = Cl and Br), was achieved by reaction with an appropriate tetra(alkyl)ammonium salt, $[\mathrm{R_4N}]\mathrm{X}$, in acetonitrile solution. The halide derivatives were characterised by IR and elemental analysis. Stirring **1** in thf for 24 h at room temperature produced a gel of poly(thf) as found for other 1,3,2,4-dithiadiazolylium salts.[12]

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Footnotes

† The compounds $\mathrm{Hg(CN)_2}$ (0.9 g, 3.8 mmol) and $[\mathrm{SNS}][\mathrm{AsF_6}]$ (2.02 g, 7.6 mmol) were placed together with a magnetic follower in one bulb of a two-limbed vessel and liquid $\mathrm{SO_2}$ (7 ml) was condensed on. After stirring (24 h) a white solid remained under a pale yellow solution. Solvent removal and a single wash with $\mathrm{CH_2Cl_2}$ afforded a white powder (2.87 g, 96%) which analysed as $[\mathrm{Hg}(\overline{\mathrm{CNSNS}})_2][\mathrm{AsF_6}]$ **1**. Elemental analyses were satisfactory (C, N, As, S, F); IR $\nu_{\mathrm{max}}/\mathrm{cm}^{-1}$: 1335 m, 1019 w, 984 m, 874 m, 766 s, 703 vs br, 583 s, 560 s, 449 s, 398 vs. Crystals suitable for single-crystal X-ray structure determination were obtained by slow addition of $\mathrm{CH_2Cl_2}$ to a saturated solution of **1** in acetonitrile.

‡ *Crystal data* for **1**: M 786.73, triclinic, space group $P\bar{1}$, $a = 5.787(3)$, $b = 7.569(4)$, $c = 9.321(5)$ Å, $\alpha = 92.23(4)$, $\beta = 95.55(5)$, $\gamma = 106.01(4)°$, $U = 389.7(4)$ Å^3, $Z = 1$, $D_c = 3.352$ g cm^{-3}, $\mu(\text{Mo-K}\alpha) = 14.75$ mm^{-1}, $F(000) = 358$, crystal size 0.45 × 0.20 × 0.04 mm. Data were collected at 160 K using a Stoe-Siemens diffractometer, Cryostream cooler[6] and Mo-Kα radiation ($\lambda = 0.71073$ Å) with $2\theta_{\mathrm{max}} = 50°$ (complete sphere of data, ω–θ scans); semi-empirical absorption corrections were applied.[7] The structure was solved by heavy atom methods and refined[8] on all 1267 F^2 values with anisotropic displacement parameters. Final $R'_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2} = 0.1257$ for all data, conventional R [on F values for 1184 data with $F_o^2 > 2\sigma(F_o^2)$] = 0.0463, goodness of fit = 1.185 on F^2 values. Atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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