Synthesis and crystal structure of an unusual bimetallic mercury–dithiolene complex

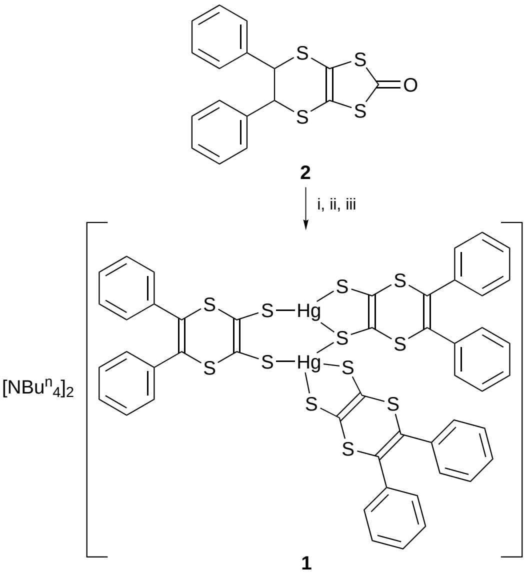
Dong-Youn Noh,[a] Allan E. Underhill*[b] and Michael B. Hursthouse[c]

[a] *Department of Chemistry, Seoul Womens University, Seoul 139-774, Korea*
[b] *Department of Chemistry, University of Wales, Bangor, Gwynedd, UK LL57 2UW*
[c] *Department of Chemistry, University of Wales, Cardiff, PO Box 912, UK CF1 3TB*

A bimetallic mercury(II) dithiolene complex in which the ligand exhibits three different modes of coordination to the mercury atoms within the same molecular species is reported.

Metal dithiolene complexes have been widely studied because of their potential in applications such as molecular conductors, ferromagnets, IR dyes, liquid crystals and catalysis.[1–3] As part of an extensive programme of research into these unusual compounds we have been studying the synthesis and properties of metal complexes of ligands derived from dmit (dmit = 1,3-dithiol-2-thione-4,5-dithiolate). During the course of these studies we have prepared a bimetallic mercury(II)–dithiolene complex **1**, which has a most unusual structure involving three differing modes of coordination by the same dithiolene ligand and contains a three-coordinate Hg^{II}. Here we report the synthesis and X-ray crystal structure of **1**.

The synthesis of the mercury–dithiolene complex **1** is outlined in Scheme 1. The 1,3-dithiole-2-one **2** was treated with KOH dissolved in MeOH under N_2 to open the five-membered ring.[5] To the solution were added separate solutions of $HgCl_2$ and TBABr in MeOH. The yellow precipitate was filtered off and washed with MeOH. The precipitate was recrystallised from acetone–ethyl acetate in a freezer to yield **1**† in 32% yield. Surprisingly, the precursor (or an intermediate thereof) has undergone oxidative dehydrogenation during this reaction to yield the fully conjugated system 1,4-dithiacyclohexadiene observed in **1**.



Scheme 1 *Reagents and conditions*: i, KOH, MeOH, room temp.; ii, $HgCl_2$, MeOH then [NBu$^n_4$]Br, MeOH; iii, recrystallization from acetone–ethyl acetate, 32% yield

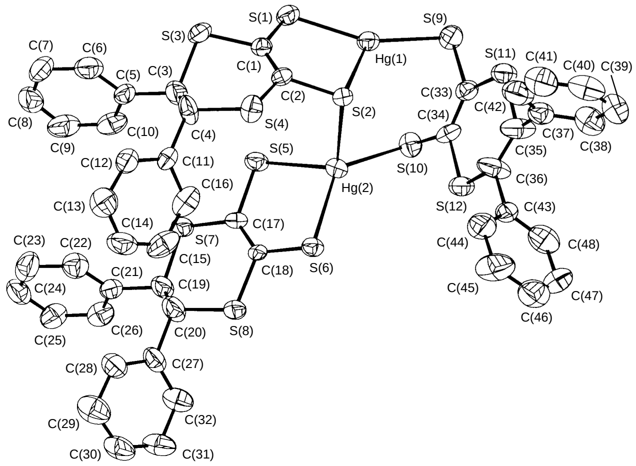


Fig. 1 The single-crystal X-ray structure of [NBu$^n_4$][Hg_2(dithiolene)$_3$], with ellipsoids shown at 50% probability and [NBu$^n_4$]$^+$ ions omitted. For clarity only mercury and sulfur atoms are labelled, with all other atoms being carbon. Selected bond lengths (Å) and angles (°): Hg(1)–S(1) 2.367(3), Hg(1)–S(2) 2.609(2), Hg(1)–S(9) 2.348(3), Hg(2)–S(2) 2.748(2), Hg(2)–S(5) 2.502(2), Hg(2)–S(6) 2.484(2), Hg(2)–S(10) 2.481(3); S(1)–Hg(1)–S(2) 88.31(8), S(1)–Hg(1)–S(9) 155.40(8), S(2)–Hg(1)–S(9) 115.24(7), S(2)–Hg(2)–S(5) 108.31(8), S(2)–Hg(2)–S(6) 114.44(8), S(2)–Hg(2)–S(10) 95.26(9), S(5)–Hg(2)–S(6) 88.52(7), S(5)–Hg(2)–S(10) 120.97(8), S(6)–Hg(2)–S(10) 129.47(10).

The crystal structure of **1**‡ and selected interatomic parameters are presented in Fig. 1 and show two mercury atoms bridged and chelated by three dithiolene ligands, each of which have different binding modes. One ligand simply chelates a mercury ion, [Hg(2)], whilst another ligand acts as a normal μ_2 bridge between Hg(1) and Hg(2) and the final ligand chelates Hg(1) and further bridges *via* one sulfur to Hg(2). As far as we are aware these variations in ligand behaviour (and indeed the resulting formations of oligomers) are unique in the area of dithiolate chemistry, but similar features are known in β-diketonate clusters.[6] The two mercury centres are in different coordination environments. Hg(1) is three coordinate with a very distorted trigonal planar geometry which is due to the ligand bonding constraints. Hg(2) however is four coordinate with very distorted tetrahedral geometry. These multiple forms of coordination have introduced considerable strain into the complex, as may be seen upon investigation of the Hg–S bond lengths. the conventionally coordinated ligand produces expected bond lengths [Hg(2)–S(5), Hg(2)–S(6)]. However around Hg(1) a longer bond is observed for the bridging sulfur [S(2)] and a shortening is seen for the chelating sulfur atoms [S(3), S(9)]. A lengthening is also observed for the Hg(2)–S(2) bridging sulfur, whilst the Hg(2)–S(10) bond has the expected length.

We thank the EPSRC and KOSEF for financial support.

Footnotes and References

* E-mail: CH5013@bangor.ac.uk

† Selected analysis data for **1**, yellow crystal (from acetone–ethyl acetate), mp 180–181 °C. Elemental analysis: calc. C, 51.11; H, 5.47; N, 1.49; S, 20.42 for $C_{80}H_{102}Hg_2N_2S_{12}$; observed. C 51.04, H 5.89, N 1.11, S 21.34%. FTIR (KBr, cm^{-1}): 1479.9, 1451.4, 1378.0 (C=C), 765.8, 718.8, 694.6, (C–H phenyl) 513.5, 435.4, 408.8.

‡ *Crystal data*: $C_{80}H_{102}Hg_2N_2S_{12}$, M_r = 1877.54, triclinic, space group $P1$ (no. 2), a = 12.144(2), b = 12.219(2), c = 29.588(8) Å, α = 96.82(4), β = 91.326(9), γ = 99.380(5)°, U = 4297.3(14) Å, Z = 2, D_c = 1.451 g cm^{-3}, $F(000)$ = 1896, μ(Mo-Kα) = 3.90 cm^{-1}. Data were collected at 293(2) K, for a crystal of dimensions 0.24 × 0.24 × 0.215 mm, on a FAST TV Area detector diffractometer following previously described procedures. 12291 data were recorded and merged to give 8421 unique (R_{int} = 0.0669). The structure was solved *via* heavy-atom methods (SHELX),[8] to give two independent molecules in the asymmetric unit and then refined by full-matrix least squares on all $F_0{}^2$ data (SHELX-93).[9] An absorption correction was applied using DEFABS.[10] The final R, R_w indices [$I > 2\sigma(I)$] were 0.0368, 0.0710 for 873 parameters (non-hydrogen atoms anisotropic hydrogen atoms in idealised positions, C–H = 0.96 Å, with U_{iso} tied to U_{eq} of the parent atoms). CCDC 182/620.

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Received in Cambridge, UK, 4th September 1997; 7/06460H