Novel vinylation of a mercury(II) centre in $[S_2WS_2HgCl_2]^{2-}$ by acetone: synthesis and structure of $[PPh_4]_2[S_2WS_2Hg(CH{=}CH_2)_2]\cdot 0.5Me_2CO$ and its topochemical conversion into $[PPh_4]_2[S_2WS_2Hg(C{\equiv}CH)_2]\cdot 0.5MeCHO$

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Reaction of $[PPh_4]_2[S_2WS_2HgCl_2]$ with acetone affords a yellow vinyl complex $[PPh_4]_2[S_2WS_2Hg\ (CH{=}CH_2)_2]\cdot 0.5Me_2CO$ which on standing in a desiccator for 3–4 months transforms to a black ethynyl derivative $[PPh_4]_2[S_2WS_2Hg(C{\equiv}CH)_2]\cdot 0.5MeCHO$.

Polymetallic sulfido complexes have stimulated profound research interest due to their solid-state properties, applications in catalysis and structural similarity and/or functional analogy to the biosites of metal–sulfur metalloenzymes.[1] The enhancement of electronic communication[2] between the adjacent metal sites in S,S-bridged linear heteropolymetallic complexes containing MS_4^{2-} (M = Mo, W) ions as terminal and/or bridging ligands[2–4] has led to isolation of several organometallic tetrathiometallate complexes[2,4] which are interesting catalytic precursors[1,5] having implications in organic and organometallic synthesis.[6] Although several mixed cyano–tetrathiometallate complexes of copper(I) and silver(I) are known,[7] no mixed complex of zinc, cadmium and mercury has yet been reported.[8] During our attempt to synthesize a mixed cyano-tetrathiometallate mercury(II) complex, a new compound $[PPh_4]_2[S_2WS_2HgCl_2]$ **1**[†] was isolated which on reaction with acetone yielded a yellow product subsequently characterized as $[PPh_4]_2[S_2WS_2Hg(CH{=}CH_2)_2]\cdot 0.5Me_2CO$ **2**.[†] Upon standing in a desiccator, **2** underwent a topochemical conversion to a black ethynyl derivative, $[PPh_4]_2[S_2WS_2Hg(C{\equiv}CH)_2]\cdot 0.5MeCHO$ **3**.[†]

Here we report the first example of vinylation of a metal centre by acetone in synthesising complex **2** from **1**, and spontaneous dehydrogenation of the ethenyl complex, **2**, to an ethynyl complex, **3**, in the solid state.

The gradual disappearance of the $\nu_{C=O}$ vibration of acetone, with simultaneous growth of $\nu_{C\equiv C}$ and an out-of-plane C–H deformation (of CHO)[9] vibration in the IR spectra of **2** as a function of time (Fig. 1) clearly shows the transformation of **2** into **3**. The ^{13}C NMR [75.5 MHz, $(CD_3)_2SO$ $SiMe_4$] chemical shifts of **2** at δ 117.1 and 118.3 are due to β-carbon atoms of the coordinated vinyl group[10] while that for the α-carbon atom, observed at δ 151,[10] is broad and unresolved. The authenticity of the assignments of ^{13}C signals has been confirmed by *J*-modulated spin–echo for ^{13}C coupled to ^1H, which is used to determine the number of attached protons to carbon. Weak ^{13}C signals at δ 64.5 and 102.0 in **3** are due to the β- and α-carbon atoms, respectively, of the coordinated ethynyl group.[10] The ^1H [300 MHz, $(CD_3)_2SO$] signals of the acetone and acetaldehyde molecules occurring in the crystal lattices of **2** and **3** have been observed at δ 3.28 (d, 6 H, *J* 11.6 Hz) and 9.1 (s, 1 H, –CHO) respectively, the corresponding signals for the ethenyl (in **2**) and

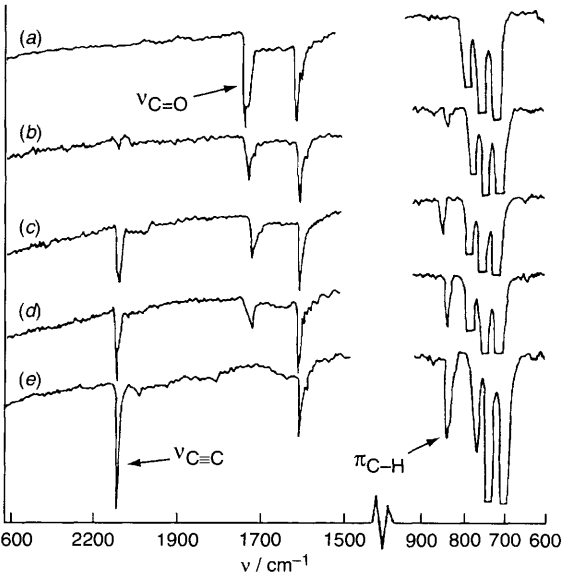

Fig. 1 Change of the IR spectra of **2** with time showing the disappearance of $\nu_{C=O}$ of acetone, and emergence of $\nu_{C\equiv C}$ and π_{C-H} of –CHO; 0 (*a*), 45 (*b*), 75 (*c*), 90 (*d*) and 120 days (*e*). Vibrations of the phenyl groups of PPh_4^+ are also shown for reference.

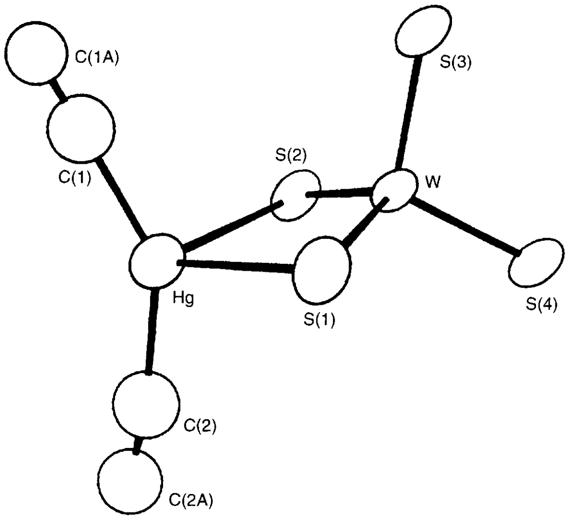

Fig. 2 An ORTEP view of the anion of **2** with selected bond distances (Å) and angles (°): Hg–W 3.299(1), W–S(1) 2.210(6), W–S(2) 2.217(6), W–S(3) 2.172(6), W–S(4) 2.156(6), Hg–S(1) 2.724(6), Hg–S(2) 2.743(6), Hg–C(1) 2.04(2), Hg–C(2) 2.04(2), C(1)–C(1A) 1.30(2), C(2)–C(2A) 1.29(2), S(1)–Hg–S(2) 82.9(2), S(1)–W–S(2) 109.6(2), S(3)–W–S(4) 109.0(2), C(1)–Hg–C(2) 143(1), W–S(1)–Hg 83.2(2), W–S(2)–Hg 82.7(2), Hg–C(1)–C(1A) 169(2), Hg–C(2)–C(2A) 176(2)

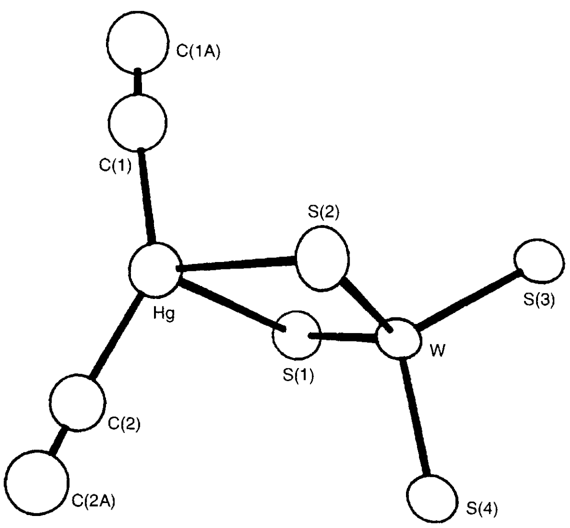

Fig. 3 An ORTEP view of the anion of **3** with selected bond distances (Å) and angles (°): Hg–W 3.295(2), W–S(1) 2.206(8), W–S(2) 2.217(8), W–S(3) 2.178(8), W–S(4) 2.142(8), Hg–S(1) 2.728(8), Hg–S(2) 2.738(9), Hg–C(1) 2.05(3), Hg–C(2) 2.00(3), C(1)–C(1A) 1.16(3), C(2)–C(2A) 1.15(3), S(1)–Hg–S(2) 82.9(2), S(1)–W–S(2) 109.8(3), S(3)–W–S(4) 108.2(3), C(1)–Hg–C(2) 147(2), W–S(1)–Hg 83.1(2), W–S(2)–Hg 82.7(2), Hg–C(1)–C(1A) 177(4), Hg–C(2)–C(2A) 172(4)

ethynyl (in **3**) groups are however not observed at room temperature probably due to fluxionality.[11]

The molecular structures of **2** and **3**, determined by X-ray crystallography,‡ consist of heterobinuclear anionic units of $[S_2WS_2Hg(CH{=}CH)_2]^{2-}$ in 2 and $[S_2WS_2Hg(C{\equiv}CH)_2]^{2-}$ in **3**, PPh_4^+ cations and disordered acetone (**2**) or acetaldehyde (**3**) molecules in the lattice. The ORTEP views of the anions of **2** and **3** are shown in Figs. 2 and 3. The anion geometries in **2** and **3** are best described as two edge-condensed tetrahedra. In both the dimers W atoms with two bridging and two terminal sulfido (S^{2-}) ligands display nearly tetrahedral coordination while each Hg atom is bonded to two terminal carbon atoms and two bridging sulfur atoms to complete a highly distorted tetrahedral (HgS_2C_2) kernel. The asymmetry in the WS_2Hg bridge is reflected in the Hg–S_b[12] and W–S_b[13] bond lengths. The Hg–C and C–C bond distances of the coordinated ethenyl (in **2**) and ethynyl (in **3**) groups are well within the expected ranges.[14] The positive and negative ion FAB-MS spectroscopic data§ also corroborate the structural analyses.

The mechanisms of conversions **1** → **2** and **2** → **3** are not yet fully understood. Further investigations in this area are continuing.

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Footnotes

† **1** was synthesized by reacting $HgCl_2{\cdot}2H_2O$ (0.33 mmol) with KCN (0.66 mmol) in aqueous media followed by addition of PPh_4Cl (0.67 mmol) and $[NH_4]_2WS_4$ (0.4 mmol); yield, 65%. IR(KBr) ν/cm^{-1}: (W–S_t) 490, 480; W–S_b + Hg–S_b 440 (br); (Hg–Cl) 420; this rather high wavenumber is characteristic for the Hg–Cl vibrations.[15] **2** was obtained by slow crystallization of **1** from spectroscopic grade acetone–light petroleum (bp 40–60 °C); yield, 51.8%. The same product could also be obtained if acetone alone was used as the solvent. IR(KBr) ν/cm^{-1}: (W–S_t) 485, 480; (M–S_b) 440, 435; (C=O of acetone) 1720. Conversion of **2** into **3** starts after *ca.* 10–15 d and is completed in *ca.* 120 d to yield **3**. Black crystals obtained from the corresponding yellow crystals remain diffractible; yield, 98.5%. IR(KBr) ν/cm^{-1}: (W–S_t) 490, 480; (M–S_b) 440 (br); (C≡C) 2080; π(C–H) of –CHO 830. Satisfactory elemental analyses (C, H, S, Hg, W, Cl) were obtained for all the isolated complexes. Electronic spectra of the complexes were very similar, and typical for WS_4-coordinated d^{10} metal complexes[7] (*ca.* 450, 390 and 270 nm).

‡ *Crystal data* for **2**: $[PPh_4]_2[S_2W(\mu\text{-}S)_2Hg(CH{=}CH_2)_2]{\cdot}0.5Me_2CO$, $C_{53.5}H_{49}HgO_{0.5}P_2S_4W$, M = 1274.5, yellow, monoclinic, space group $P2_1/n$, a = 17.703(3), b = 13.240(3), c = 23.632(5) Å, β = 110.83(3)°, U = 5177(2) Å^3, Z = 4, μ = 5.44 mm^{-1}, $F(000)$ = 2488, D_c = 1.635 g cm^{-3}, D_m = 1.65 g cm^{-3}. 3453 observed [$I > 2\sigma(I)$] reflections ($2 < 2\theta < 42$°), Nicolet R3m/V diffractometer. Mo-Kα (λ = 0.71073 Å), R_1 = 0.064, wR_2 (on F^2) = 0.209, gof = 1.169.

For **3**: $[PPh_4]_2[S_2W(\mu\text{-}S)_2Hg(C{\equiv}CH)_2]{\cdot}0.5MeCHO$, $C_{53}H_{44}HgO_{0.5}P_2S_4W$, M = 1263.5, black, monoclinic, space group $P2_1/c$, a = 17.678(7), b = 13.258(5), c = 23.910(9) Å, β = 112.75(4)°, U = 5168(3) Å^3, Z = 4, μ = 5.45 mm^{-1}, $F(000)$ = 2456, D_c = 1.624 g cm^{-3}, D_m = 1.62 g cm^{-3}. 2714 observed [$I > 2\sigma(I)$] reflections ($3 < 2\theta$ 45°) Enraf-Nonius CAD 4 diffractometer, Mo-Kα (λ = 0.71073 Å), R_1 = 0.068, wR_2 (on F^2) = 0.197, GOF = 1.201. The intensity data for **2** and **3** were corrected for Lorentz-polarization and absorption (based on Ψ-scans) factors. The structures were solved and refined by Patterson (SHELX 76[16]), successive Fourier and full-matrix least-squares methods (SHELXL 93[17]): anisotropic thermal parameters for all non-hydrogen atoms (anionic carbon and disordered solvent atoms isotropic), the H-atom positions were calculated geometrically. 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.

§ FAB-MS (NBA/Magic TFA): negative ion-mode; For **2**, m/z 958 $\{(PPh_4)_2[M(C_2H_3)_2]\}^-$, 537 $[M(C_2H_3)]^-$, 280 $\{\frac{1}{2}[M(C_2H_3)_2]^{2-}\}$ positive ion-mode; for **2** m/z 1274 $\{(PPh_4)_2[M(C_2H_3)_2(CH_3)_2CO]\}^+$; for **3**, m/z 1240 $[(PPh_4)_2M(C_2H)(C_2H_2)]^+$, 1273 $[(PPh_4)_2M((C_2H)C_2H_5CHOP)]^+$ (M = WS_4Hg).

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