The Melding of Dithiocarbamate and Alkyne Moieties at Molybdenum Centres; New Ligands and Heterometallacyclic Complexes

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The reactions of $[Mo_2(\mu\text{-}S_2)_2(S_2CNEt_2)_4](BF_4)_2$ and $MoO(S_2)(S_2CNR_2)_2$ with dimethyl acetylenedicarboxylate result in the formation of orange and green heterometallacyclic complexes containing the novel organosulfur 2-sulfanylethenylthiomethylidene(*N*,*N*-dialkyl)ammoniumato-*C*,*S*,*S*′ and 2,3-η-1,3-disulfanylprop-2-enylidene(*N*,*N*-dialkyl)-ammoniumato-*S*,*S*′ ligands.

The reactions of alkynes and other unsaturated organic molecules with sulfur-containing ligands have attracted considerable interest due to the importance of carbon–sulfur and carbon–carbon bond making and breaking processes in the synthesis of fine chemicals, bulk industrial chemicals, and fuels.[1–3] A variety of unusual carbon- and sulfur-containing ligands have been formed by reactions of 1,1-dithio complexes and alkynes; coupling, fragmentation and rearrangement processes feature in these reactions.[4–6] Here, we report the melding of dithiocarbamate and alkyne moieties to generate novel organosulfur ligands and heterometallacyclic complexes, as well as an unusual isomerisation involving the new compounds.

Reaction of $[Mo_2(\mu\text{-}S_2)_2(S_2CNEt_2)_4](BF_4)_2$[7,8] with excess dimethyl acetylenedicarboxylate (DMAC) in refluxing 1,1,2-trichloroethane resulted in the formation of air-stable orange **1a**, green **2a** and as yet unidentified red products; the course of the reaction was conveniently monitored by thin layer chromatography and the products could be separated by column chromatography. These compounds were also produced by the reaction of $MoO(S_2)(S_2CNEt_2)_2$[9] and DMAC in refluxing 1,2-dichloroethane. Similarly, reaction of $MoO(S_2)(S_2CNMe_2)_2$[9] and DMAC permitted the synthesis of the methyl derivatives, orange **1b** and green **2b**. Compounds **1** were slowly converted to **2** in hot (*ca.* 100 °C) inert solvents or more rapidly upon melting. The formulae of the compounds were established by microanalytic and mass spectrometric results. Analyses were consistent with the stoichiometry '$MoS_2(DMAC)_2(S_2CNR_2)_2$' and indicated that the expected formation of one ene-1,2-dithiolato ligand had been accompanied by the incorporation of a second DMAC molecule into the products. Observation of parent ions with *m*/*z* 687 for **1b** and **2b** and *m*/*z* 741 for **1a** and **2a** indicated that all compounds were monomeric, consistent with their formation from $MoO(S_2)(S_2CNR_2)_2$ and the cleavage of $[Mo_2(\mu\text{-}S_2)_2(S_2CNEt_2)_4]^{2+}$ upon reaction. Spectroscopic data† were consistent with the structures established by X-ray crystallography (*vide infra*). The ^1H NMR spectrum of **1b** exhibited four N–CH_3 resonances and three CO_2CH_3 resonances. Two of the N–CH_3 resonances were considerably broadened due to site exchange on the NMR timescale. The $^{13}C\{^1H\}$ NMR spectrum of **1b** exhibited 15 resonances, consistent with the equivalence of some carbon resonances. Resonances at δ 116.7 and 228.2 were assigned to –SC=C and $CSCNMe_2$ atoms, respectively [C(3) and C(1), Fig. 1]. The ^1H NMR spectrum of **2b** revealed a non-fluxional molecule with C_1 symmetry; all methyl groups were inequivalent. The $^{13}C\{^1H\}$ NMR spectrum of **2b** exhibited resonances at δ 53.4 and 89.9, assigned to the carbon centres in a heteroallylic fragment [C(3) and C(4), respectively, Fig. 2]. The NMR spectra of **1a** and **2a** exhibited similar features. The electronic spectra of orange **1a** and **1b** were virtually identical, consistent with their having analogous structures; this was also true of green **2a** and **2b**.

The structures of **1a** (Fig. 1) and **2b** (Fig. 2) were established by X-ray crystallography.‡ Seven-coordinate **1a** is composed of a dithiocarbamato-*S*,*S*′ ligand, an ene-1,2-dithiolato-*S*,*S*′ ligand and a 2-sulfanylethenylthiomethylidene(*N*,*N*-diethyl)-ammoniumato-*C*,*S*,*S*′ ligand formed by the melding of dithiocarbamate and alkyne moieties; the complex possesses a highly irregular coordination geometry. The bidentate ligands are essentially planar with bond distances and angles typical of these ligands.[10] In the generation of the novel *C*,*S*,*S*′-donor ligand, fragmentation of a dithiocarbamato ligand provides the S and $SCNEt_2$ fragments incorporated in a 1,2-fashion across the alkyne triple bond. The Mo–S(1) bond is considerably longer than the other Mo–S bonds in the molecule; the Mo–C(1) bond distance is 1.969(4) Å. Acute angles characterise the Mo–S(1)–C(1) triangle and a particularly small S(1)–Mo–C(1) angle is associated with the bidentate S(1)–C(1) fragment. The Mo–C(1)–N(1) angle is 149.0(3)°. Both the Mo–S(1)–C(3)–C(4)–S(2) and Mo–S(1)–C(1)–N(1)–C(7,9) fragments are nearly planar and the dihedral angle between these planes is 82.3°. The trigonal geometry at N(1), the short C(1)–N(1) distance, and the small dihedral angle of 9.3° between the Mo–S(1)–C(1) and N(1)–C(7,9) planes are consistent with a degree of π-bonding between N(1) and C(1). The C(1) atom is 2.84 Å from S(6) and 2.91 Å from S(2).

Eight-coordinate **2b** also exhibits a highly irregular coordination geometry. In common with **1a**, this complex contains a dithiocarbamato-*S*,*S*′ and an ene-1,2-dithiolato-*S*,*S*′ ligand. The ene-1,2-dithiolato ligand of **2b** is planar but it is swivelled toward the dithiocarbamato ligand about the S···S vector. Also, **2b** contains a novel 2,3-η-1,3-disulfanylprop-2-enylidene(*N*,*N*-dimethyl)ammoniumato-*S*,*S*′ ligand. Three

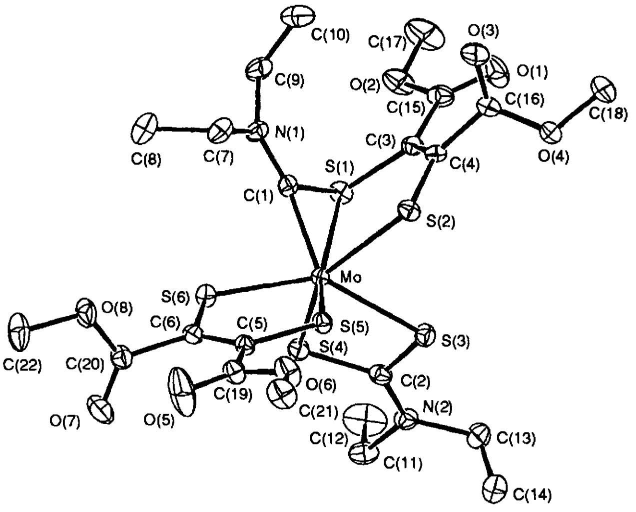

Fig. 1 Molecular structure of **1a**. Selected bond lengths (Å) and angles (°): Mo–S(1) 2.519 (1), Mo–S(2) 2.456 (1), Mo–S(3) 2.470 (1), Mo–S(4) 2.471 (1), Mo–S(5) 2.306 (1), Mo–S(6) 2.360 (1), Mo–C(1) 1.969 (4), C(1)–N(1) 1.292 (5), S(1)–C(1) 1.754 (4), S(1)–C(3) 1.768 (4), C(3)–C(4) 1.335 (5), C(4)–S(2) 1.691 (4), S(3)–C(2) 1.701 (4), S(4)–C(2) 1.702 (4), C(2)–N(2) 1.296 (5), S(5)–C(5) 1.705 (4), S(6)–C(6) 1.696 (4), C(5)–C(6) 1.343 (5), C(1)–Mo–S(1) 43.9 (1), S(1)–Mo–S(2) 81.83 (4), Mo–C(1)–S(1) 84.9 (2), N(1)–C(1)–Mo 149.0 (3), N(1)–C(1)–S(1) 125.0 (3), C(1)–S(1)–C(3) 101.3 (2), Mo–S(1)–C(1) 51.1 (1), Mo–S(2)–C(4) 105.4 (1), S(3)–Mo–S(4) 69.16 (4), S(5)–Mo–S(6) 80.60 (4).

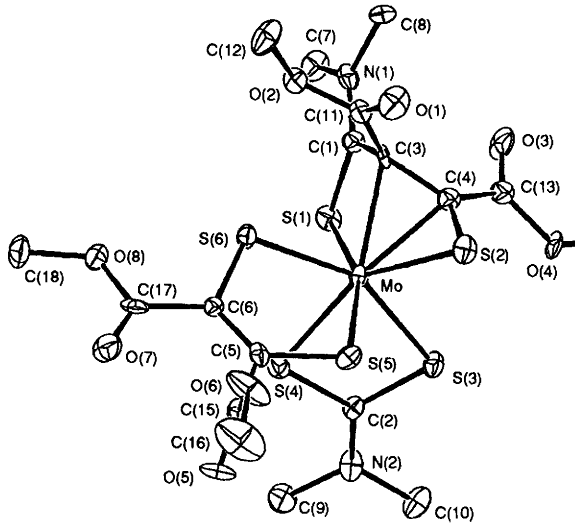

Fig. 2 Molecular structure of **2b**. Selected bond lengths (Å) and angles (°): Mo–S(1) 2.531 (3), Mo–S(2) 2.341 (3), Mo–S(3) 2.527 (3), Mo–S(4) 2.502 (3), Mo–S(5) 2.384 (3), Mo–S(6) 2.310 (3), Mo–C(3) 2.26 (1), Mo–C(4) 2.17 (1), S(1)–C(1) 1.68 (1), C(1)–N(1) 1.31 (1), C(1)–C(3) 1.45 (2), C(3)–C(4) 1.43 (1), C(4)–S(2) 1.72 (1), S(3)–C(2) 1.71 (1), S(4)–C(2) 1.70 (1), C(2)–N(2) 1.30 (1), S(5)–C(5) 1.69 (1), C(5)–C(6) 1.33 (1), S(6)–C(6) 1.73 (1), S(1)–Mo–C(3) 64.8 (3), C(3)–Mo–C(4) 37.6 (4), C(4)–Mo–S(2) 44.7 (3), S(3)–Mo–S(4) 68.3 (1), S(5)–Mo–S(6) 83.2 (1), Mo–S(1)–C(1) 83.9 (4), S(1)–C(1)–C(3) 110.6 (9), C(1)–C(3)–Mo 100.0 (7), C(1)–C(3)–C(4) 114 (1), C(3)–C(4)–C(13) 121 (1), S(2)–C(4)–C(3) 115.1 (9), Mo–C(4)–C(13) 127.9 (8), Mo–C(3)–C(11) 116.4 (8).

planar fragments may be identified within the disulfanylprop-2-enylidene ligand. The planarity of the S(1)–C(1)–C(3)–N(1)–C(7,8) moiety and the C(1)–N(1) distance of 1.31(1) Å are consistent with considerable π-character in the C(1)–N(1) bond. The trigonal geometries of C(3) and C(4), the significant dihedral angle of 38.3° between the trigonal planes, the short C(3)–C(4) and C(4)–S(2) bond distances and the apparent heteroallylic η^3-*C,C′,S* binding mode of the C(3)–C(4)–S(2) fragment are consistent with electronic delocalization within this fragment.

A number of canonical structures may be drawn for the new ligands, and heterometallacyles **1** and **2**. In all cases, delocalised bonding must pertain. Compounds **1** are best described as thio(dialkylamino)methylidene species. They could be envisaged to result from initial attack of a dithiocarbamato sulfur atom on an alkyne carbon, followed by S–CN bond cleavage, the formation of the second S–C bond and the coordination of the CNR_2 carbon atom to the metal. Since **1** are converted to **2** upon heating, it is probable that they result from an isomerization in which the R_2NC fragment spanning the Mo–S bond migrates and inserts into an S–C= bond.

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Footnotes

† *Selected spectroscopic data.* **1b**: IR ν(CN)/cm^{-1} 1544 m, 1500 m; ν(CO)/cm^{-1} 1730 s, 1705 s. ^{1}H NMR (300 MHz, $CDCl_3$): δ, 2.84 (s, br, 3H, CH_3), 3.07, 3.18 (s, 3H, 2 CH_3), 3.62 (s, br, 3H, CH_3), 3.84, 3.94 (s, 6H, 4 CO_2CH_3). $^{13}C\{^1H\}$ NMR: δ, 39.3, 39.7 (s, CH_3), 44.6, 48.4 (s, br, CH_3), 52.9, 53.1, 53.3 (s, CO_2CH_3), 116.7 (s, CSC=), 152.8, 163.6, 163.8, 165.5, 168.4 (s, 4 CO_2CH_3 + 3 SC=), 197.8 (s, S_2CNMe_2), 228.2 ($SCNMe_2$). **2b**: IR ν(CN)/cm^{-1} 1586 m, 1532 m; ν(CO)/cm^{-1} 1698 s. ^{1}H NMR (400 MHz, CD_2Cl_2): δ, 3.00, 3.12, 3.41, 3.40 (s, 3H, CH_3), 3.58, 3.87, 3.88, 3.94 (s, 3H, CO_2CH_3). $^{13}C\{^1H\}$ NMR: δ, 39.2, 39.5, 40.0, 41.8 (s, CH_3), 52.4, 52.5, 52.9, 53.2 (s, CO_2CH_3), 53.4 (s, CC=CS), 89.9 (s, CC=CS), 152.6, 164.5, 167.3, 169.5, 169.9, 170.9 (s, 4CO_2CH_3 + 2 SC=), 194.6, 197.8 (s, $CNMe_2$).

‡ *Crystal Data* for **1a**: $C_{22}H_{32}MoN_2O_8S_6$, M = 740.8, triclinic space group $P\bar{1}$, a = 10.662(3), b = 16.999(4), c = 8.605(3) Å, α = 90.97(2)°, β = 95.33(2)°, γ = 91.78(2)°, V = 1551.7(7) Å^3, Z = 2, ρ_{calc} = 1.585 g cm^{-3}, $F(000)$ = 760, μ(Mo-Kα) = 8.71 cm^{-1}, crystal dimensions 0.08 × 0.11 × 0.35 mm, $R(R_w)$ = 0.038 (0.043) for 6204 unique reflections [$I \geqslant 3.0\sigma(I)$] and 352 variables.

2b: $C_{18}H_{24}MoN_2O_8S_6$, M = 684.7, orthorhombic space group $P2_12_12_1$, a = 15.955(9), b = 23.24(1), c = 7.68(1) Å, V = 2849(4) Å^3, Z = 4, ρ_{calc} = 1.596 g cm^{-3}, $F(000)$ = 1392, μ(Mo-Kα) = 9.41 cm^{-1}, crystal dimensions 0.13 × 0.13 × 0.24 mm, $R(R_w)$ = 0.040 (0.047) for 1812 unique reflections [$I \geqslant 3.0\sigma(I)$] and 296 variables.

Data collected with a Rigaku AFC6R diffractometer using Mo-Kα radiation. Structures solved by direct methods and refined by a full-matrix least-squares procedure. The absolute configuration of **2b** was determined by comparing the refinement of the other hand. 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.

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