

A series of μ -Disulphido-Dimolybdenum(IV) Complexes: X-Ray Structure of the Novel (μ -Tetrahydrothiophene) Complex $[(C_4H_8S)Cl_3Mo(\mu-S_2)(\mu-C_4H_8S)MoCl_3(C_4H_8S)]$

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The complexes $[Mo_2(\mu-S_2)Cl_6L_3]$ ($L = C_4H_8O$ or C_4H_8S); $[Mo_2(\mu-S_2)Cl_6L_2]$ ($L = C_4H_8O$, MeCN, 4-MeOC₆H₄CN, 2-MeC₅H₄N, or 2,6-Me₂C₅H₃N) and $[PPh_4]_2[Mo_2S_2Cl_6]$ have been prepared; the X-ray structure of $[(C_4H_8S)Cl_3Mo(\mu-S_2)(\mu-C_4H_8S)MoCl_3(C_4H_8S)]$ shows an unusual bridging C_4H_8S ligand.

Complex compounds of molybdenum with sulphur ligands are of fundamental importance in the search for understanding of the structure and function of nitrogenase and of molybdenum-catalysed processes such as hydrodesulphurisation.¹ In the context of the latter processes, complexes of molybdenum sulphides with thiophene derivatives are of particular interest. As part of our investigation of molybdenum complexes with sulphur, dinitrogen, and hydride ligands,² we have obtained a new series of ($\mu-S_2$)-dimolybdenum complexes which show novel features and may provide useful starting materials for further synthesis. We were interested in obtaining complexes with the S_2^{2-} ligand because of its synthetic potential in the build-up of multi-metal centres, particularly involving molybdenum and iron.³

A number of ($\mu-S_2$) complexes of molybdenum have been prepared,^{1,4} but their co-ordination chemistry has been little explored. Here we report a series of ($\mu-S_2$) complexes with a variety of co-ligands at the metal centres, including, unusually, bridging C_4H_8S .

Our synthetic route was to treat $[Mo(CO)_6]$ with S_2Cl_2 in dichloromethane, to give a dark, brown-green material, analysing as $Mo_2S_2Cl_6 \cdot CH_2Cl_2$ which on treatment with ligands, L , gives the series of diamagnetic adducts $[Mo_2(\mu-S_2)Cl_6L_3]$ ($L = C_4H_8S$ or C_4H_8O ; green), $[Mo_2(\mu-S_2)Cl_6L_2]$ ($L = C_4H_8O$, MeCN, 4-MeOC₆H₄CN, 2-MeC₅H₄N, or 2,6-Me₂C₅H₃N; brown). The green tris-adducts are of relatively low solubility and precipitate from the reaction solution; the brown adducts were isolated by concentration of the mother liquor. Addition of $[PPh_4]Cl$ gives $[PPh_4]_2[Mo(\mu-S_2)Cl_6]$ (pale brown). The complexes show $\nu(S_2)$ in the region 590–640 cm^{-1} of their i.r. spectra.

We have obtained green crystals of $[Mo_2(\mu-S_2)Cl_6(C_4H_8S)_3]$ and its molecular structure (Figure 1)[†] shows it to have, in

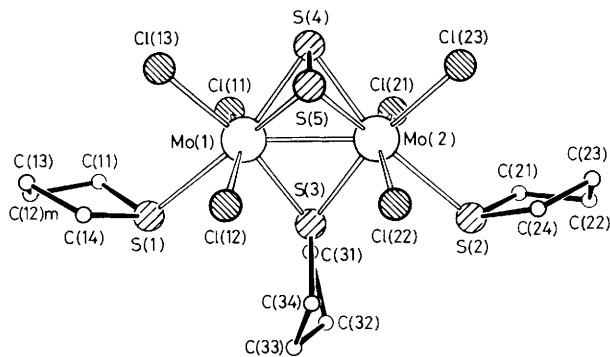


Figure 1. Structure of $[(C_4H_8S)Cl_3Mo(\mu-S_2)(\mu-C_4H_8S)MoCl_3(C_4H_8S)]$, showing arrangement of major occupation in disordered region about C(12)m. Principal bond dimensions (\AA and $^\circ$); where no e.s.d.s are given (values in parentheses), e.s.d.s are less than 0.5 in the least significant digit: Mo(1)–Mo(2) 2.769; Mo(1)–S(1) 2.641(1); Mo(1)–S(3) 2.390(1); Mo(1)–S(4) 2.401(1); Mo(1)–S(5) 2.405(1); Mo(1)–Cl 2.405(1)–2.418(1); Mo(2)–S(2) 2.644(1); Mo(2)–S(3) 2.391(1); Mo(2)–S(4) 2.408(1); Mo(2)–S(5) 2.414(1); Mo(2)–Cl 2.389(1)–2.408(1); S(4)–S(5) 1.991(1); Mo(1)–S(3)–Mo(2) 70.8; Mo(1)–S(4)–Mo(2) 70.3; Mo(1)–S(5)–Mo(2) 70.1.

[†] *Crystal Data* for $[(C_4H_8S)Cl_3Mo(\mu-S_2)(\mu-C_4H_8S)MoCl_3(C_4H_8S)]$, $C_{12}H_{24}Cl_6Mo_2S_5$, $M = 733.2$, orthorhombic, space group $Pbca$ (No. 61), $a = 20.315(7)$, $b = 18.179(6)$, $c = 13.105(4)$ \AA , $U = 4839.6$ \AA^3 , $Z = 8$, $D_c = 2.012$ $g\ cm^{-3}$, $F(000) = 2896$, $\mu(Mo-K_\alpha) = 21.0$ cm^{-1} , $\lambda(Mo-K_\alpha) = 0.71069$ \AA . The crystal was a dark green square prism, mounted on glass fibre in air. Preliminary photographic examination was followed by measurements on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-radiation for accurate cell dimensions (25 centred reflections with θ ca. 10.5°) and intensity data (4246 unique reflections, 722 with $I < 2\sigma$, θ range 1.5 – 25°); corrections for Lorentz-polarisation effects, absorption, and negative intensities. Structure solution from Patterson, electron density, and difference maps for all atoms (except H atoms about disordered CH_2 site in one terminal C_4H_8S ligand). Full-matrix least-squares refinement (SHELX⁸) on all atoms; all non-H-atoms anisotropic, H-atoms independent and isotropic except in disordered region. At convergence, $R = 0.029$, $R_w = 0.026$ for all 4246 reflections weighted $w = \sigma_F^{-2}$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

addition to the (μ -S₂) and two terminal C₄H₈S ligands, the unusual μ -C₄H₈S ligand.

The structure can be described as consisting of two molybdenum centres having distorted pentagonal bipyramidal co-ordination, which share a common face. The structure is similar to that of the related complex ion⁵ [Mo₂(μ -S₂)(μ -SO₂)(CN)₈]²⁻ and clearly a family of such μ -S₂, μ -L bridged complexes is to be expected. It should be noted that a related series of C₄H₈S-bridged compounds exists for niobium and tantalum,⁶ and the complex⁷ [(Me₂S)Cl₂Mo(μ -Me₂S)(μ -Cl)₂MoCl₂(SMe₂)] is a member of the same family of compounds.

The μ -S₂²⁻ and μ -C₄H₈S ligands form a triple sulphur bridge between molybdenum atoms; the S-S bond distance [1.991(1) Å] is shorter than that of free S₂²⁻ (2.13 Å) and in the range commonly found in molybdenum complexes.^{1,4,5} The μ -C₄H₈S ligand is symmetrically disposed between the molybdenum atoms and the bridging Mo-S distance [mean 2.391(1) Å] (*trans* to Cl) is less than that of the terminal C₄H₈S ligands [mean 2.643(2) Å] (*trans* to S₂²⁻). The Mo-Mo distance (2.769 Å) is in the range (2.70–2.85 Å) generally observed in (μ -S₂)-molybdenum complexes and a molybdenum-molybdenum bonding interaction is a possible but inessential reason for the diamagnetism of these Mo^{IV} compounds.

Presumably the green C₄H₈O analogue has bridging tetrahydrofuran, but the brown [Mo₂Cl₆L₂] series have S₂²⁻ bridges only; further structural studies are being undertaken to clarify this point.

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