

Photoinduced Insertion of Sulphur Bridges into a $\text{Cr}\equiv\text{S}\equiv\text{Cr}$ Multiple Bond, and X-Ray Crystal Structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\mu\text{-S})_2(\mu\text{-S}_2)$

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Photoinduced insertion of sulphur ligands into the $\text{Cr}\equiv\text{S}\equiv\text{Cr}$ multiple bond of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{S}$ provides a novel route to the new complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2\text{S}_4$, which has one bidendate $\mu\text{-S}_2$ and two $\mu\text{-S}$ bridges symmetrically placed between the $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}$ moieties.

Studies on transition metal-sulphur complexes remain an area of intense research efforts.^{1,2} In view of the current interest shown in the structure and reactivity of the $(\text{cp})_2\text{M}_2\text{S}_4$ complexes (cp = $\eta^5\text{-C}_5\text{H}_5$), particularly with regard to the great diversity in bonding modes of the sulphur ligands,³⁻⁶ we herein report the structure of $(\text{cp})_2\text{Cr}_2\text{S}_4$ (**1**) formed by an unusual insertion of sulphur bridges into the linear $\text{Cr}\equiv\text{S}\equiv\text{Cr}$ multiple bond of the $(\text{cp})_2\text{Cr}_2(\text{CO})_4\text{S}$ complex.

Irradiation (-30 to -10 °C, 2×150 W tungsten filament lamp, 9 h) of a yellow-green solution of $(\text{cp})_2\text{Cr}_2(\text{CO})_4\text{S}$ (1.24 mmol), prepared *in situ* as described,² in tetrahydrofuran (THF; 50 ml) containing sulphur (6.25 mmol) produced a suspension of fine dark solids (0.20 g) of unchanged S and $(\text{cp})_4\text{Cr}_4\text{S}_4$ (ca. 40% yield) in a brown mother liquor containing unchanged $(\text{cp})_2\text{Cr}_2(\text{CO})_4\text{S}$ and $(\text{cp})_2\text{Cr}_2\text{S}_4$ (**1**), together with minor amounts of $(\text{cp})_4\text{Cr}_4\text{S}_4$ and an unknown species (cp ¹H n.m.r. absorptions at δ 4.36, 5.72, 4.91, and 5.13, respectively for the four aforementioned complexes). Column chromatography on silica gel and then neutral alumina gave the starting $(\text{cp})_2\text{Cr}_2(\text{CO})_4\text{S}$ (0.55 mmol, 44%) and (**1**) (0.166 mmol, 13%). A purple-red solution of (**1**) in toluene produced fine black air-stable needles at -30 °C; complex (**1**)

was characterised *via* elemental analysis, spectroscopic data,[†] and X-ray crystallography.[‡]

The salient feature of the molecular structure, shown in

[†] Selected spectral data: n.m.r. ¹H(C_6D_6), δ 5.72 (s, C_5H_5); ¹³C(C_6D_6) 100.94 (s, C_5H_5); *m/z* 362 ($\text{cp}_2\text{Cr}_2\text{S}_4$), 298 ($\text{cp}_2\text{Cr}_2\text{S}$), 233 (cpCr_2S_2), and 181 (cpCrS_2); i.r. (KBr): ν 3110w, 3090w, 1630w,br, 1420m, 1050vw, 1010m, 910vw,br, 850sh,vw, 830sh,m, 815s, and 500vw cm^{-1} .

[‡] Crystal data for (**1**): $(\text{C}_5\text{H}_5)_2\text{Cr}_2\text{S}_4$, $M_r = 362.44$, monoclinic, space group $P2_1/c$, $a = 10.608(6)$, $b = 6.924(2)$, $c = 17.733(7)$ Å, $\beta = 90.08(4)^\circ$, $U = 1302.5(8)$ Å³, $D_m = 1.85(1)$ g cm^{-3} , $Z = 4$, $D_c = 1.848$ g cm^{-3} , Mo- K_α radiation (graphite-monochromatized), $\lambda = 0.71069$ Å, $\mu = 22.16$ cm^{-1} , $T = 295$ K, empirical absorption correction ($\mu_r = 0.20$, transmission factors 0.492 to 0.613), 2057 unique reflections ($2\theta_{\text{max}} = 50^\circ$), 1733 observed [$|F_o| > 3\sigma(|F_o|)$], $R = 0.046$, $R_w = 0.056$, $S = 1.267$ with $w = [\sigma^2(|F_o|) + 0.001|F_o|^2]^{-1}$. The structure was solved and refined using SHELXTL.⁷ Non-H atoms were varied anisotropically, and H atoms were generated geometrically and allowed to ride on their respective parent C atoms with assigned isotropic thermal parameters. 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.

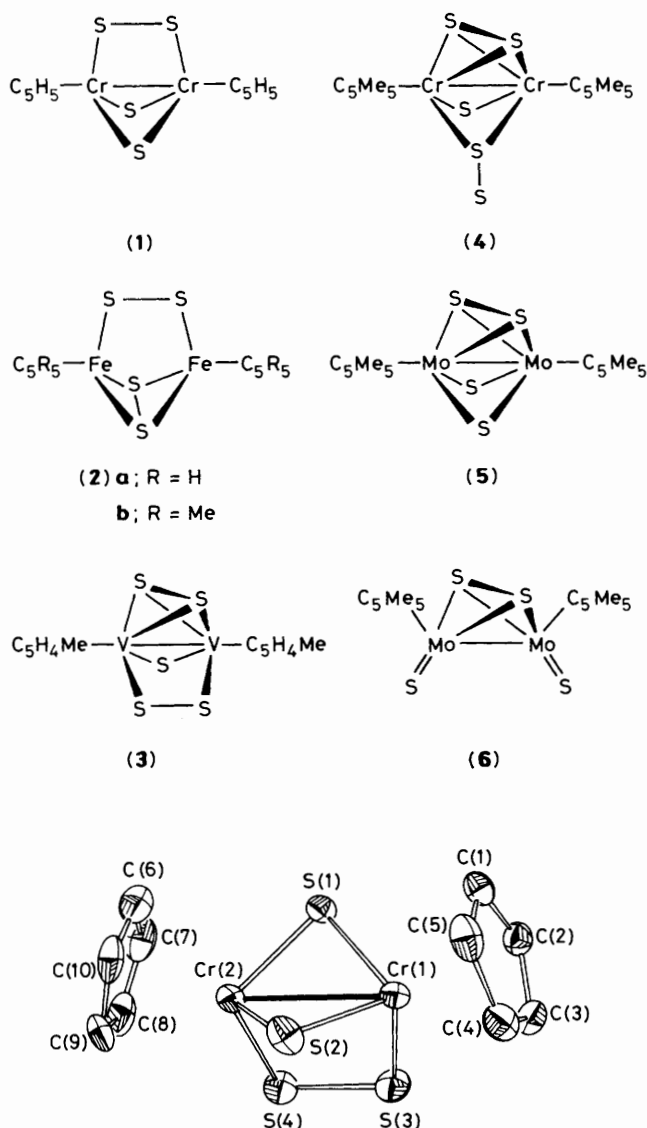


Figure 1. Perspective view of the molecular structure of complex (1), showing the atom numbering scheme and approximate C_{2v} molecular symmetry. Selected bond lengths (Å) and angles ($^{\circ}$): Cr(1)–Cr(2), 2.807(1); Cr(1)–S(1), 2.202(2); Cr(2)–S(1), 2.195(2); Cr(1)–S(2), 2.198(2); Cr(2)–S(2), 2.200(2); Cr(1)–S(3), 2.220(2); Cr(2)–S(4), 2.223(2); S(3)–S(4), 2.028(2); Cr(1)–C(1), 2.254(6); Cr(1)–C(2), 2.233(6); Cr(1)–C(3), 2.212(6); Cr(1)–C(4), 2.231(6); Cr(1)–C(5), 2.251(6); Cr(2)–C(6), 2.242(7); Cr(2)–C(7), 2.223(7); Cr(2)–C(8), 2.199(8); Cr(2)–C(9), 2.227(7); Cr(2)–C(10), 2.238(7); S(1)–Cr(1)–S(2), 91.5(1); S(1)–Cr(2)–S(2), 91.6(1); S(1)–Cr(1)–S(3), 99.2(1); S(1)–Cr(2)–S(4), 99.3(1); S(2)–Cr(1)–S(3), 100.2(1); S(2)–Cr(2)–S(4), 99.4(1); Cr(1)–S(1)–Cr(2), 79.3(1); Cr(1)–S(2)–Cr(2), 79.3(1); Cr(1)–S(3)–S(4), 99.8(1); Cr(2)–S(4)–S(3), 100.4(1).

Figure 1, is the planar Cr–S–S–Cr bridge of type IIb in Müller's classification¹ in the Cr_2S_4 core of approximate C_{2v} symmetry. Though bidentate μ -S₂ bridges have been reported before, in complexes (2a)^{6b} and (2b),³ in which there was no metal–metal interaction, and in complex (3),⁸ in these examples it was oriented perpendicularly to a second doubly bidentate μ -S₂ ligand. The structure of (1), containing one bidentate μ -S₂ and two μ -S ligands, has only one exact parallel in $(\eta^5\text{-Pr}^i\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_4$,⁴ but this type of bonding is unknown for a group 6 element. In fact, it is entirely different from that

predicted^{6b} based on the known structures of $(\text{C}_5\text{Me}_5)_2\text{Cr}_2\text{S}_5$ (4)⁹ and the isomers (5) and (6) of $(\text{cp})_2\text{Mo}_2\text{S}_4$.^{5a,b} It might be expected that (1), like (4) and (5), would have all the S atoms lying in a plane perpendicular to the M–M bond.

The Cr–Cr separation of 2.807(1) Å is appropriate for a single bond, as found also in the case of the cubane-like $(\text{cp})_4\text{Cr}_4\text{S}_4$ complex (av. 2.857 Å)¹⁰ and $(\text{cp})_2\text{Cr}_2\text{Fe}_2(\mu_3\text{-CO})_2(\mu_3\text{-S})_2(\text{CO})_6$ (av. 2.775 Å).¹¹ The S–S bond distance of 2.028 Å, though shorter than the Pauling single bond length of 2.10 Å, closely resembles that in $(\eta^5\text{-Pr}^i\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_4$,⁴ and lies within the range observed for disulphur ligands.¹ The averaged Cr–S bond distances, 2.199(2) Å for the μ -S groups and 2.222(2) Å for the μ -S₂ group, are very short, in fact, ca. 0.04 and 0.075 Å shorter than the respective distances in $(\text{cp})_2\text{Cr}_2\text{S}_5$,⁹ and ca. 0.05–0.26 Å shorter than Cr–S separations in other complexes.^{2,10} This lends support to the postulation of synergic σ and π bonding between the S and Cr atoms.¹² Indeed, to enable each of the metal–metal bonded Cr atoms to attain the favoured 18e configuration, the μ -S and μ -S₂ ligands would be required to provide three more π electrons in addition to the three σ electrons to each metal centre.

From the reactivity standpoint, $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Cr}_2\text{S}_4$ has been reported to be formed *via* S-atom abstraction from $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Cr}_2\text{S}_5$ using PPh_3 ,¹³ but the insertion of additional sulphur ligands into a presumably inert $\text{M}\equiv\text{S}\equiv\text{M}$ group,¹⁴ thereby converting the linear multiply bonded S into one of a bent μ -S type or a μ -S₂ type, as found in the structure of (1), is unprecedented and highlights the versatility in reactivity patterns of M–S bonds.

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