# Sulphur Chromium Complexes: Syntheses and Crystal Structures of ($\eta^5$-$C_5H_5)_2Cr_2(CO)_4S$ and ($\eta^5$-$C_5H_5)_2Cr_2(CO)_5S_2$

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The facile reaction of dicyclopentadienylhexacarbonyldichromium with stoicheiometric amounts of elemental sulphur in tetrahydrofuran or toluene at ambient temperature produces ($\eta^5$-$C_5H_5)_2Cr_2(CO)_4S$ (**1**) and ($\eta^5$-$C_5H_5)_2Cr_2(CO)_5S_2$ (**2**) in isolated yields of 100 and 90%, respectively.

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Transition metal–sulphur complexes are of current interest, both because of their biological and catalytic implications and, also, because of the remarkable versatility of the $S_2$ ligand in bonding modes and its demonstrated potential in the synthesis of new metal cluster complexes.[1,2] However, other than for Mo, Mn, and Fe, sulphur complexes of the transition metals have only occasionally been reported.[1–4] Recently, the only chromium–sulphur complex reported, ($\eta^5$-$C_5Me_5)_2Cr_2S_5$, was found to illustrate three different modes of M–S bonding.[3] We now describe the syntheses and structures of two further Cr–S complexes, ($\eta^5$-$C_5H_5)_2Cr_2(CO)_4S$ (**1**) and ($\eta^5$-$C_5H_5)_2Cr_2(CO)_5S_2$ (**2**).

($\eta^5$-$C_5H_5)_2Cr_2(CO)_4S$
(**1**)

($\eta^5$-$C_5H_5)_2Cr_2(CO)_5S_2$
(**2**)

[($\eta^5$-$C_5H_5)Cr(CO)_3]_2$ reacts rapidly with a 1/8 molar proportion of $S_8$ per dimer molecule in tetrahydrofuran (THF) or toluene under an inert atmosphere at ambient temperature to give (**1**) as dark green needle-shaped crystals (m.p. 111—112 °C), in 100% isolated yield. With 2/8 molar proportions or more of $S_8$, (**2**) was obtained as fine dark brown crystals in 90% yield. Both complexes (**1**) and (**2**) are air-stable as solids and have been characterised by *X*-ray diffraction and by total elemental analyses. Spectral characteristics are given in Table 1.

Crystals of (**1**), suitable for single crystal *X*-ray diffraction analysis, were obtained as needles from a solution in hexane–ether at −17 °C overnight. Crystals of (**2**) were obtained as dark brown rectangular prisms with curved faces from a solution in THF–pentane after *ca.* 20 days at −78 °C.

*Crystal data:* (**1**), $C_{14}H_{10}Cr_2O_4S$, $M = 378.29$, triclinic, space group $P\bar{1}$, $a = 21.405(7)$, $b = 10.308(3)$, $c = 8.167(3)$ Å, $\alpha = 90.76(2)$, $\beta = 97.22(2)$, $\gamma = 59.49(2)$°, $U = 1535.2$ Å$^3$, $D_m = 1.69(3)$, $D_c = 1.636$ g cm$^{-3}$, $Z = 4$, $\mu$(Mo-$K_{\bar{\alpha}}$) $= 14.92$ cm$^{-1}$, $\lambda = 0.7107$ Å, $T = 293(1)$ K. (**2**), $C_{15}H_{10}Cr_2O_5S_2$, $M = 438.36$, monoclinic, space group $P2_1/n$, $a = 11.638(4)$, $b = 15.508(5)$, $c = 9.825(3)$ Å, $\beta = 111.56(2)$°, $U = 1649.2$ Å$^3$, $D_m = 1.75(2)$, $D_c = 1.765$ g cm$^{-3}$, $Z = 4$, $\mu$(Cu-$K_{\bar{\alpha}}$) $= 135.32$ cm$^{-1}$, $\lambda = 1.5418$ Å, $T = 293(1)$ K.

2981 unique reflections for (**1**) [$I > 2.5\sigma(I)$, $3° < 2\theta < 50°$, Mo-$K_{\bar{\alpha}}$] and 1729 unique reflections for (**2**) [$I > 2.5\sigma(I)$, $3° < 2\theta < 120°$, Cu-$K_{\bar{\alpha}}$] were measured on a Philips PW1100/20 diffractometer. The structure of (**1**) was solved with MULTAN[5] and refined by blocked-matrix least-squares methods with SHELX[6] to $R = 0.051$ and $R_w = 0.049$. The structure of (**2**) was solved from Patterson and Fourier syntheses and was refined by full-matrix least-squares analysis (SHELX) to $R = 0.067$ and $R_w = 0.071$. All cyclopentadienyl groups in both structures exhibited rotational disordering between two sites and were included in the scattering model as rigid planar groups (C–C = 1.378 Å, C–H = 0.97 Å) with isotropic thermal parameters. All other atoms were assigned anisotropic thermal parameters. Molecular structures are shown in the ORTEP[7] diagrams (Figures 1 and 2). For clarity only that ring

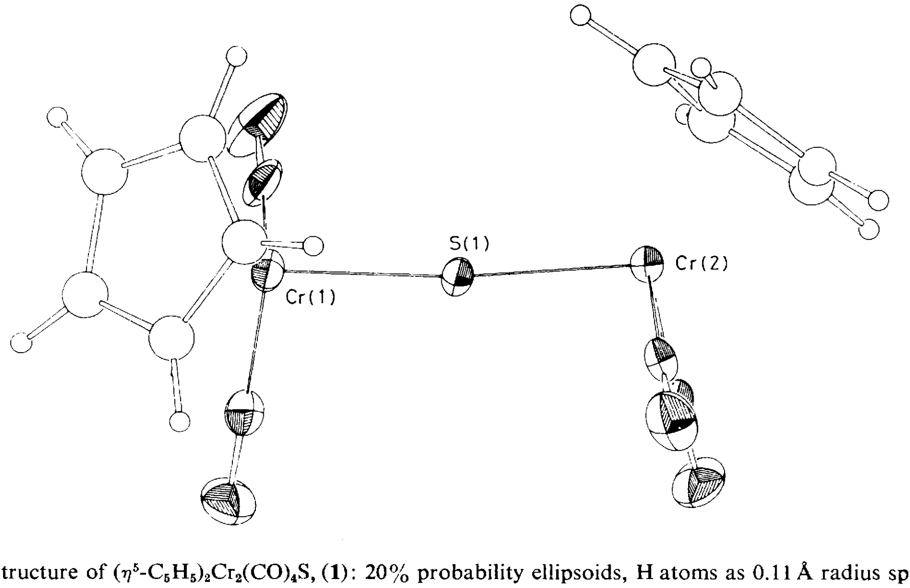

**Figure 1.** Molecular structure of ($\eta^5$-$C_5H_5)_2Cr_2(CO)_4S$, (**1**): 20% probability ellipsoids, H atoms as 0.11 Å radius spheres (both figures).

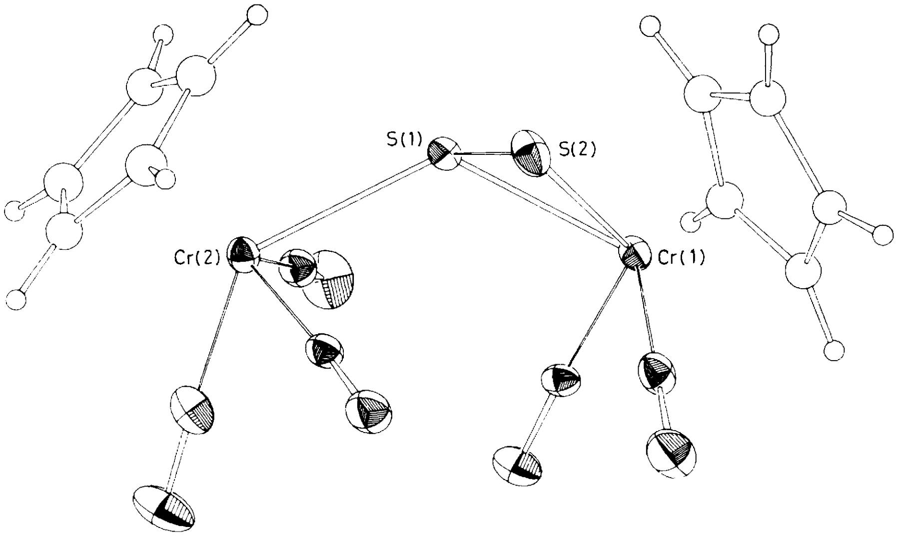

**Figure 2.** Molecular structure of $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_5S_2$, (**2**). Bond angles at sulphur are: Cr(1)–S(1)–Cr(2) 125.8(1), Cr(1)–S(1)–S(2) 66.3(1), Cr(1)–S(2)–S(1) 63.7(1), Cr(2)–S(1)–S(2) 115.5(1)° and at chromium: S(1)–Cr(1)–S(2) 50.1(1)°.

**Table 1.** Spectral characteristics of (**1**) and (**2**).

| | N.m.r. | | I.r.[c] | | Mass spectra |
|---|---|---|---|---|---|
| | $^1H(\delta)$[a] | $^{13}C(\delta)$[b] | $\nu_{CO}/cm^{-1}$ | Other bands, $\nu/cm^{-1}$ | $m/z$ |
| $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4S$ (**1**) | 4.36 (s) | 89.20 (s, $C_5H_5$)<br>246.71 (s, CO)[f] | 1994vs, 1955vs, 1938vs, 1916s, sh, 1906vs, 1885vs | 815s, 637s, 613s, 601m, sh, 552m, 533s, 520m, sh, 485sh, 477s | 377.9110[d] |
| $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_5S_2$ (**2**) | 4.14 (s) | 91.39 (s, $C_5H_5$)<br>[g] | 2014vs, 1969vs, 1939vs, 1924s, 1919s, 1852vs, 1821w, sh | 850w, 824m, 639m, 627w, sh, 615m, 575s, 549s, 522m, 502w, 484w, 465vw, 415vw | [e] |

[a] Chemical shifts referred to $Me_4Si$ in $C_6D_6$ or $CD_3C_6D_5$. [b] Chemical shifts referred to TMS in [$^2H_8$]toluene($Me_4Si$ in $CD_3C_6D_5$). [c] Measured in KBr disk. vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [d] Calc. 377.9110. [e] Molecular ion not observed. Significant mass fragments observed were $m/z$ 377.9110 for $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4S$, 321.9214 for $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_2S$ (calc. 321.9212), 293.9258 for $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)S$ (calc. 293.9263), 265.9314 for $(\eta^5\text{-}C_5H_5)_2Cr_2S$ (calc. 265.9313), 200.91 for $(\eta^5\text{-}C_5H_5)Cr_2S$, 182.03 for $(\eta^5\text{-}C_5H_5)_2Cr$, and 135.86 for $Cr_2S$, all of which were also observed in the mass spectrum of (**1**). [f] 247.6 (s) at 183 K. [g] Too labile at room temperature to permit unambiguous assignment of CO resonances.

of each cyclopentadienyl pair having the preferred (highest occupancy factor) orientation is shown.[†]

In (**1**) the two Cr atoms are linked by a single $\mu$-S bridge, the ligand arrangement about each metal atom being of the three-legged piano-stool type found in $(C_6Me_6)Cr(CO)_3$.[8] This is the first example of a binuclear Cr complex based on the $Cr_2S$ unit, *i.e.* a *single* bridging sulphur. The Cr–$\mu$-S distances [2.067(2)—2.076(2) Å] are noticeably shorter than those in $(\eta^5\text{-}C_5Me_5)_2Cr_2S_5$ [av. 2.238(3) Å].[3] Indeed, the $Cr_2S$ unit [Cr–S (av.) = 2.072(2)Å, Cr–S–Cr (av.) = 174.4(2)°] is structurally very similar to the $Mo_2S$ unit in $[(CN)_6MoSMo(CN)_6]^{6-}$ [Mo–S = 2.173(1) Å, Mo–S–Mo = 169.5(2)°][9] and, as in the Mo complex, the unusually short Cr–S bonds are probably due to the presence of S→M $\pi$-bonding interactions.[10] The parallel–antiparallel dispositions of the carbonyl groups are also consistent with the presence of Cr–S double-bonding. The observation of only one $^{13}C$ (carbonyl) resonance in the n.m.r. spectra at both 25 and 183 K (Table 1) suggests that the barrier to rotation about the Cr–S–Cr axis is small.

Compound (**2**) comprises the first example of a chromium–sulphur complex based on the $Cr_2S_2$ unit. The most noteworthy structural feature is the simultaneous end-on and side-on bonding of the $S_2$ ligand, *i.e.* the $S_2$ unit functions as an unsymmetrical bridge between the two Cr atoms, S(1) being bound to both Cr(1) and Cr(2) [Cr–S = 2.348(2) and 2.466(2) Å respectively] while S(2) is bound only to Cr(1) [Cr–S = 2.399(2) Å]. This bonding feature, of type Ib in Müller's classification,[1,2] is the first of its kind for a chromium complex and the third of its kind among the transition metals {after $[Mo_4(NO)_4(S_2)_5S_3]^{4-}$ which possesses four such groups[11] [S–S (av.) = 2.048(7) Å, Mo–S = 2.465(5)—2.492(5) Å] and $(\eta^5\text{-}C_5H_5)_2Fe_2(S_2)_2(CO)$[12] [S–S (av.) = 1.993(8), Fe–S = 2.230(6)—2.293(6) Å]}. The S–S distance in (**2**) [2.009(2) Å] is close to the above values and to that in octasulphur (2.060 Å).[13] The co-ordination geometry around Cr(2) is of the four-legged piano stool type with the metal atom having an $18e^-$ configuration completed *via* one six- and four two-electron donor ligands. In contrast, Cr(1) is electron deficient ($16e^-$) and is best envisaged as having three-legged piano stool co-ordination geometry with a single $\pi$(L)–d(M) $\sigma$-bond to the $\eta^2$-bonded $S_2$ group.

Apart from the interesting structural features exhibited by these molecules the very facile reactions giving rise to them show considerable potential as model desulphurisation reactions.

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[†] Refined occupancy factor ratios for the disordered cyclopentadienyl pairs range from 6:1 to 1.3:1. Atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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## References

1 A. Müller, W. Jaegermann, and J. H. Enemark, *Coord. Chem. Rev.*, 1982, **46**, 245, and references therein.

2 A. Müller and W. Jaegermann, *Inorg. Chem.*, 1979, **18**, 2631.

3 H. Brunner, J. Wachter, E. Guggolz, and M. L. Ziegler, *J. Am. Chem. Soc.*, 1982, **104**, 1765.

4 H. Brunner, W. Meier, J. Wachter, E. Guggolz, T. Zahn, and M. L. Ziegler, *Organometallics*, 1982, **1**, 1107.

5 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 1971, **27**, 368.

6 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge.

7 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee.

8 M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1298.

9 M. G. B. Drew, P. C. H. Mitchell, and C. F. Pygall, *J. Chem. Soc., Dalton Trans.*, 1979, 1213.

10 A. Müller, E. Diemann, R. Jostes, and H. Bögge, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 934.

11 A. Müller, W. Eltzner, and N. Mohan, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 168.

12 C. Giannotti, A. M. Ducourant, H. Chanaud, A. Chiaroni, and C. Riche, *J. Organomet. Chem.*, 1977, **140**, 289.

13 A. Caron and J. Donohue, *Acta Crystallogr.*, 1965, **18**, 562.