

Fig. 2. Atom-labelling scheme and 50% probability ellipsoids for complex *B*.

Regarding the partial presence of Cl attached to C(15) in *A* and *B*, we note that in the syntheses the source of the metal is ruthenium trichloride, which can conceivably act as a chlorinating agent like its congener ferric chloride (De La Mare & Ridd, 1959). However, the origin of the specificity of chlorine substitution at C(15) is unclear at present.

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Structure of Tetrameric η -Cyclopentadienyl Chromium Sulfide

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Abstract. Tetrakis(η -cyclopentadienyl)tetra- μ_3 -thiotetra-chromium(III), [Cr₄S₄(C₅H₅)₄], $M_r = 596.64$, $C2/c$, $a = 17.582(8)$, $b = 8.045(3)$, $c = 16.137(8)$ Å, $\beta = 116.5(4)^\circ$, $V = 2043(7)$ Å³, $Z = 4$, $D_x = 1.939$ g cm⁻³, Ni-filtered Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 216$ cm⁻¹, $F(000) = 1200$, $T = 293$ K, $R = 5.1\%$, 1560 unique reflections. The cubane struc-

ture of the tetramer can be viewed as being formed from two interpenetrating tetrahedra of chromium and sulfur atoms with each chromium coordinated to three other chromium atoms, three sulfur atoms and one η^5 -cyclopentadienyl ring. The bond lengths and angles of the cyclopentadienyl rings are normal.

Introduction. Transition-metal–sulfur cubane systems are of continuing interest on account of their biological

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and biochemical relevance (Vahrenkamp, 1975; Garner, 1980). During our studies on organo-chromium-sulfur chemistry (Goh, Hambley & Robertson, 1983), we found that thermolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4\text{S}$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_5\text{S}_2$ in refluxing toluene gave $[(\eta^5\text{-C}_5\text{H}_5)\text{CrS}]_4$ as the main product. Although this compound has been referred to on several occasions (Vahrenkamp, 1975; Garner, 1980), there has been only spectral inference on its structure (Ulm, 1961) and no X-ray diffraction analysis has been performed (Fischer, 1984). We therefore decided to solve its structure, in order to make comparisons with analogous transition-metal cubanes.

Experimental. Slow cooling of the product solution from the thermolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_5\text{S}_2$ followed by standing for 3 d at room temperature gave black rectangular prismatic crystals of $(\eta^5\text{-C}_5\text{H}_5)_4\text{Cr}_4\text{S}_4$. Selected crystal [0.075 × 0.35 × 0.1 mm; faces (100), ($\bar{1}00$), (010), (0 $\bar{1}0$), (001) and (00 $\bar{1}$)] mounted on Nicolet P3m diffractometer; 15 independent reflections, well separated in reciprocal space, computer centred to obtain orientation matrix and refine accurate cell parameters; θ -2 θ scan technique (Nicolet, 1980); 1560 unique reflections measured for h, k, l 0 to 19, 0 to 8 and -17 to 17 respectively; intensities of three standard reflections showed no significant crystal decay during entire data collection; raw intensity data corrected for Lorentz-polarization effects and absorption (max., min. transmission coefficients 0.69, 0.59) (Freyberg, Mockler & Sinn, 1976); 1234 reflections with $F_o^2 > 3\sigma(F_o^2)$, $\sigma(F_o^2)$ estimated from counting statistics (Corfield, Doedens & Ibers, 1967); systematic absences for hkl data with $h+k = 2n+1$ and $h0l$ with $l = 2n+1$ indicated space groups Cc or $C2/c$; centrosymmetric $C2/c$ shown to be correct choice by interpretation of Patterson vectors and by successful refinement of crystal structure; coordinates of two symmetrically independent chromium atoms from Paterson synthesis, which phased data sufficiently well to permit location of remaining nonhydrogen atoms from Fourier synthesis; full-matrix least-squares refinement based on F on PDP-11/45 computer (Freyberg *et al.*, 1976);* $w = [2F_o/(F_o^2)]^2$; anisotropic temperature factors introduced for nonhydrogen atoms; further difference Fourier functions permitted location of all hydrogen atoms, included in refinement for four cycles of least squares then held fixed; goodness of fit = 3.4, max. least-squares shift/e.s.d. = 0.04 in final cycle; model converged with $R = 5.1$ and $wR = 6.3\%$ for 127 parameters; final difference Fourier map showed densities $< 0.06 \text{ e } \text{\AA}^{-3}$ near chromium atoms; atomic

* *REFINE* is used for least-squares refinement, *MAP* for Fourier, Patterson and related functions, *UNICEL* for unit-cell refinement, *FIN* for final Fourier, *F* lists *etc.*, *TABLE* for tabulations of atom parameters, bond lengths and angles, *ABSN* for absorption correction.

scattering factors for all atoms from Cromer & Waber (1974), effects of anomalous dispersion for non-hydrogen atoms included in F_c using Cromer & Ibers (1974).*

Discussion. Table 1 lists the atomic coordinates and their equivalent isotropic thermal parameters. Table 2 shows the intramolecular bond distances and angles. Figs. 1 and 2 give stereoviews of the single molecule and the packing diagram respectively. Each tetramer is situated on a crystallographic twofold rotation axis and can be viewed as formed from two interpenetrating tetrahedra, one made of two symmetrically independent chromium atoms and the other of sulfur atoms. Each

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and full lists of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42798 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and their equivalent isotropic thermal parameters ($\times 10^3 \text{ \AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
Cr(1)	0.06952 (8)	0.1759 (2)	0.22661 (9)	22
Cr(2)	0.06192 (9)	0.4265 (2)	0.34472 (10)	23
S(1)	0.0804 (1)	0.4536 (3)	0.2154 (2)	27
S(2)	0.0708 (1)	0.1485 (3)	0.3668 (1)	25
C(11)	0.1791 (6)	0.001 (1)	0.2824 (7)	35
C(12)	0.1132 (6)	-0.077 (2)	0.2089 (8)	48
C(13)	0.1005 (7)	0.025 (2)	0.1306 (7)	80
C(14)	0.1576 (7)	0.158 (2)	0.1615 (8)	57
C(15)	0.2037 (6)	0.136 (2)	0.2518 (7)	42
C(21)	0.1008 (7)	0.679 (2)	0.4049 (7)	42
C(22)	0.1716 (6)	0.607 (2)	0.4079 (7)	38
C(23)	0.1895 (7)	0.467 (2)	0.4648 (8)	49
C(24)	0.1277 (9)	0.461 (2)	0.4981 (7)	57
C(25)	0.0728 (7)	0.593 (2)	0.4604 (7)	44

* U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Interatomic bond distances (\AA) and angles ($^\circ$) for the Cr_4S_4 cubane structure

Cr(1)	Cr(1 ¹)	2.862 (5)	Cr(1)	Cr(2)	2.818 (3)		
Cr(1)	Cr(2 ¹)	2.891 (6)	Cr(2)	Cr(2 ¹)	2.854 (14)		
Cr(1)	S(1)	2.256 (3)	Cr(1)	S(2)	2.263 (3)		
Cr(1)	S(2 ¹)	2.256 (10)	Cr(2)	S(1)	2.260 (4)		
Cr(2)	S(1 ¹)	2.255 (7)	Cr(2)	S(2)	2.259 (3)		
S(1)	S(2)	3.521 (4)	S(1)	S(1 ¹)	3.472 (7)		
S(1)	S(2 ¹)	3.422 (7)	S(2)	S(2 ¹)	3.469 (17)		
Cr(1 ¹)	Cr(1)	Cr(2)	61.2 (1)	Cr(1 ¹)	Cr(2)	Cr(2 ¹)	58.7 (1)
Cr(2)	Cr(1)	Cr(2 ¹)	60.0 (1)	Cr(1)	Cr(2)	Cr(1 ¹)	60.2 (1)
Cr(1)	Cr(2)	Cr(2 ¹)	61.3 (1)	Cr(1 ¹)	Cr(2)	Cr(2 ¹)	58.7 (1)
S(1)	Cr(1)	S(2)	102.3 (2)	S(1)	Cr(1)	S(2 ¹)	98.6 (2)
S(2)	Cr(1)	S(2 ¹)	100.3 (4)	S(1)	Cr(2)	S(1 ¹)	100.4 (3)
S(1)	Cr(2)	S(2)	102.3 (3)	S(1 ¹)	Cr(2)	S(2)	98.6 (3)
Cr(1)	S(1)	Cr(2)	77.2 (2)	Cr(1)	S(1)	Cr(2 ¹)	79.7 (2)
Cr(2)	S(1)	Cr(2 ¹)	78.4 (4)	Cr(1)	S(2)	Cr(1 ¹)	78.6 (3)
Cr(1)	S(2)	Cr(2)	77.1 (2)	Cr(1 ¹)	S(2)	Cr(2)	79.6 (2)
S(1 ¹)	S(1)	S(2)	58.6 (4)	S(2 ¹)	S(1)	S(2)	59.9 (4)
S(2 ¹)	S(1)	S(1 ¹)	61.4 (4)	S(1 ¹)	S(2)	S(1)	60.0 (4)
S(2 ¹)	S(2)	S(1)	58.6 (4)	S(2 ¹)	S(2)	S(1 ¹)	61.4 (4)

Symmetry code: (i) $-x, y, \frac{1}{2}-z$.

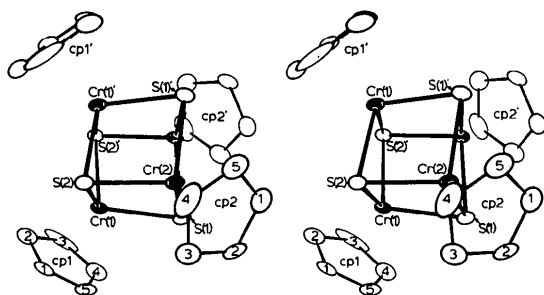


Fig. 1. Stereoview of the title compound with atom labels. The shaded spheres represent the metal atoms.

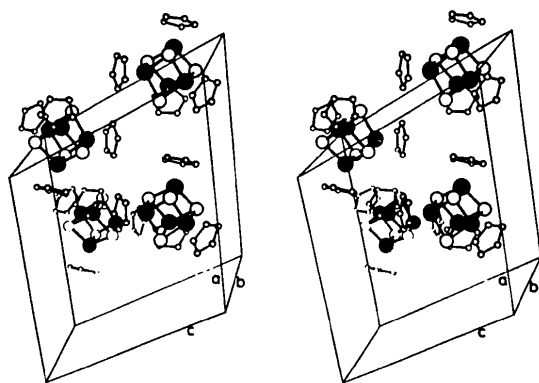


Fig. 2. The packing diagram of the unit cell. The shaded spheres represent the metal atoms.

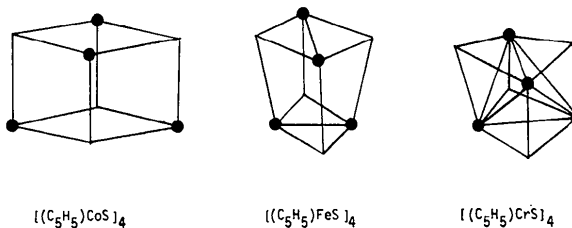


Fig. 3. Structures of M_4S_4 nuclei in the cubane complexes $[(\text{C}_5\text{H}_5)\text{MS}]_4$. The shaded spheres represent the metal atoms.

chromium atom is coordinated to three sulfur atoms, three other chromium atoms and a cyclopentadienyl ring as shown in Fig. 1. The cubane structure is distorted as a result of the difference in the sizes of the two tetrahedra. In the cobalt analogue (Simon & Dahl, 1973), no metal-metal bond is necessary to fulfil the 18-electron requirement of the cobalt atom (Vahrenkamp, 1975), the two tetrahedra are closer in size and consequently the cubane framework is only slightly distorted. In the iron analogue, however, there is one electron too few for each iron atom; this is compensated by the formation of one metal-metal bond per iron atom, a total of two iron-iron bonds in the cubane, and electron balance is thus restored. Although the sizes of the sulfur and iron tetrahedra are fairly close, the irregular iron tetrahedron causes a deformation of the overall cubane structure. A comparison of bond distances and angles is summarized in Table 3 and illustrated in Fig. 3.

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Table 3. Comparison of bond lengths and angles

	Cr	Fe*	Co†
Covalent radius (Å)	1.18	1.17	1.16
Number of metal-metal bonds per metal atom	3	1	0
Metal tetrahedron			
$M-M$ (Å)	2.857 (14)§	2.650 (6) 3.363 (16)‡	3.298 (2)§
Range (Å)	2.818-2.891	2.650-3.372	3.236-3.343
$M-M-M$ (°)‡	60.0 (1)	60.0 (1)	60.0 (1)
Range (°)	58.7-61.3	46.3-67.0	58.2-61.5
Sulfur tetrahedron			
$S-S$ (Å)	3.471 (17)§	3.334 (9)‡ 2.883 (16)§	2.990 (3)§
Range (Å)	3.422-3.521	2.874-3.334	2.950-3.048
$S-S-S$ (°)	60.0 (4)	60.0 (4)	60.0 (4)
Range (°)	58.6-61.4	54.4-70.8	58.6-61.8
$S-M$ (Å)	2.258 (10)	2.219 (11)	2.230 (2)
Range (Å)	2.255-2.263	2.198-2.252	2.226-2.234
$S-M-S$ (°)	100.4 (4)	86.5 (4)	84.34 (6)
Range (°)	98.6-102.3	80.5-98.4	82.84-86.22
$M-S-M$ (°)	78.4 (4)	90.0 (4)	95.31 (4)
Range (°)	77.1-79.7	73.7-98.2	92.86-97.23
Space group	$C2/c$	$C2/c$	$C2/c$
a (Å)	17.582 (8)	18.80 (3)	18.014 (6)
b (Å)	8.045 (3)	7.68 (1)	7.974 (2)
c (Å)	16.137 (8)	15.07 (3)	15.736 (4)
β (°)	116.5 (4)	109° 5' (20')	115.281 (9)

* Wei, Wilkes, Treichel & Dahl (1966).

† Simon & Dahl (1973).

‡ Non-bonded distances.

§ Average values.