

the Ir–H distance [*ca* 1.8 Å] to a tetrahedrally disposed *endo* H atom on C(6) [C–H = 0.95 Å] is directly comparable with those in the C–H–M bridges in [Fe( $\eta^3$ -C<sub>8</sub>H<sub>13</sub>){P(OMe)<sub>3</sub>}]<sub>3</sub>BF<sub>4</sub> (Brown, Williams, Schultz, Stucky, Iittel & Harlow, 1980), in [Mn( $\eta^3$ -C<sub>6</sub>H<sub>5</sub>Me)(CO)<sub>3</sub>] (Schultz, Teller, Beno, Williams, Brookhart, Lamanna & Humphrey, 1983) and in [Fe<sub>4</sub>( $\eta^2$ -CH)(H)(CO)<sub>12</sub>] (Beno, Williams, Tachikawa & Muettterties, 1980) [1.80–1.87 Å; all neutron diffraction studies]; and (iv) omission of the bridging H atom [H(6B)] from the scattering model (followed by reconvergence) results in a significant increase in  $wR$  [0.0339 to 0.0342; ratio significant at better than 99.5% confidence level (Hamilton, 1965)]. Omission of H(6B) from the scattering model also generates a well defined difference Fourier peak [ $\Delta\rho \approx 0.5 \text{ e } \text{Å}^{-3}$ ] 1.7 Å from Ir, 1.4 Å from C(6) and 0.5 Å from H(6B). The peak persists [ $\Delta\rho \approx 0.4 \text{ e } \text{Å}^{-3}$ ] to become the dominant feature of a  $(\sin\theta)/\lambda < 0.3 \text{ Å}^{-1}$  map, but is further displaced from the H(6B) site [ $\Delta = 0.6 \text{ Å}$ ]. The displacement results largely from the persistence (in the difference maps) of the pseudo-mirror plane at  $z = 0$ . The calculated H(6B) sites lies just 0.42 Å from the  $z = 0$  plane and the residual peak lies on that plane.

Although the exact location of the bridging H atom is unknown, the known geometry of C(6) dictates a strong interaction. Crabtree *et al.* (1985) have suggested  $r_{bp} = d_{bp} - r_M$  as a measure of the interaction strength [ $d_{bp}$  is the metal to C–H bond-pair centroid distance and  $r_M$  is the metal-atom covalent radius]. For the title complex (with C–H = 1.08 Å),  $d_{bp} \approx 1.9 \text{ Å}$  and  $r_{bp} \approx 0.6 \text{ Å}$ . Both values are at the 'strong' end of the Crabtree *et al.* (1985) compilation. The C–H–M angle ( $\approx 106^\circ$ ) is similar to those [96, 99°] in [Mo<sub>2</sub>( $\eta$ -C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>16</sub>H<sub>25</sub>)<sub>2</sub>]<sup>+</sup> (Green, Norman & Orpen, 1981) and [Fe<sub>2</sub>( $\eta$ -C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>(CO)(CH<sub>3</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]<sup>+</sup> (Dawkins, Green, Orpen & Stone, 1982), both of which exhibit similarly strong agostic interactions to  $\beta$  C–H groups [ $r_{bp} = 0.61, 0.65 \text{ Å}$ ; Crabtree *et al.* (1985)] to that in the title complex.

Except for F(1)···H(6A) [2.5 Å] all ion···ion contacts are close to or exceed the normal van der Waals separations.

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## Structure of Tris(diethyldithiophosphinato)chromium(III)

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**Abstract.** [Cr{S<sub>2</sub>P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}]<sub>3</sub>,  $M_r = 511.67$ , triclinic,  $P\bar{1}$ ,  $a = 9.638$  (1),  $b = 10.017$  (3),  $c = 13.983$  (3) Å,  $\alpha = 86.25$  (2),  $\beta = 75.15$  (1),  $\gamma = 66.95$  (1)°,  $V =$

1199.8 (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.39 \text{ g cm}^{-3}$ ,  $D_x = 1.416$  (1) g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 11.86 \text{ cm}^{-1}$ ,  $F(000) = 534$ ,  $T = 298 \text{ K}$ , 5795 X-ray

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intensities were measured on a four-circle diffractometer. Least-squares refinement gave  $R = 0.032$  for 3201 unique observed reflections [ $I > 3\sigma(I)$ ]. The Cr atom is coordinated by six S atoms from three ligands in a distorted octahedral environment [Cr-S average 2.442 (8) Å]. The average twist angle  $\varphi$  between opposite triangular faces of the octahedra along the pseudo-threefold axis is 47.2 (8)°.

**Introduction.** Chromium(III) complexes with alkyl- and aryl-substituted dithiophosphinate and dithiophosphate ligands have been extensively studied by spectroscopic methods (e.g. Wasson, Wolterman & Stoklasa, 1973) and by magnetic measurements (e.g. Cavell, Byers & Day, 1971; Hertel & Kuchen, 1971). According to these measurements the CrS<sub>6</sub> octahedra are not affected by changes in the substituents on the P atom. For example the  $\mu_{\text{eff}}$  values range from 3.88 to 3.96 BM\* for a wide range of substituents (Kuchen & Rohrbeck, 1972). Until now only one X-ray crystal structure determination of a chromium(III) complex with this type of ligand has been reported, [Cr{S<sub>2</sub>P(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}<sub>3</sub>] (Schousboe-Jensen & Hazell, 1972). In relation to our interest in the magnetic behaviour of dithiochelatate complexes, we have undertaken a crystal structure analysis of [Cr{S<sub>2</sub>P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}<sub>3</sub>] to determine the effect on the structure of replacement of the OC<sub>2</sub>H<sub>5</sub> with a C<sub>2</sub>H<sub>5</sub> group.

**Experimental.** The title compound was prepared as described by Kuchen, Metten & Judat (1964). Crystals were grown from a dioxan solution by slow evaporation, yielding thin blue plates; approximate dimensions of the crystal used 0.25 × 0.20 × 0.02 mm.  $D_m$  measured pycnometrically in cyclohexane. Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å),  $\omega/2\theta$  scan,  $\Delta\omega = 0.6^\circ + 0.5^\circ \tan\theta$ . Unit cell from least-squares fit of 25 reflections with  $12 < \theta < 25^\circ$ . Data were corrected for Lorentz and polarization effects. Absorption correction (numerical integration) for crystal defined by 6 faces, (210), ( $\bar{2}\bar{1}0$ ), ( $\bar{5}\bar{1}0$ ), (010), {001}, grid 14 × 12 × 4, transmission factor 0.78–0.98. Three standard reflections measured every half hour showed no significant variation, 5795 reflections measured, 4193 unique,  $R_{\text{int}} = 0.027$ , 3201 with  $I > 3\sigma_c(I)$  used in refinement,  $\sigma_c(I)$  based on counting statistics. Index range  $h 0 \rightarrow 11$ ,  $k -11 \rightarrow 11$ ,  $l -16 \rightarrow 16$  and  $h -6 \rightarrow 0$ ,  $k -7 \rightarrow 7$ ,  $l -10 \rightarrow 10$ ;  $2\theta_{\text{max}} = 50^\circ$ .

The structure was solved by Patterson methods and subsequent electron-density difference maps; all H atoms were located. Least-squares refinement; function minimized  $\sum w(|F_o| - |F_c|)^2$ ,  $w = [\sigma_c^2(F_o) + (0.02F_o)^2 + 0.3]^{-1}$ . The H atoms were refined with  $U_{\text{iso}}(\text{methylene}) = 0.098$  (5) and  $U_{\text{iso}}(\text{methyl}) =$

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{\text{eq}}$
Cr	0.23271 (6)	0.74259 (5)	0.73039 (4)	0.0424 (2)
S(1)	0.44083 (9)	0.75684 (9)	0.59439 (7)	0.0481 (3)
S(2)	0.07196 (9)	0.88451 (9)	0.62151 (7)	0.0495 (3)
S(3)	0.27041 (10)	0.50284 (9)	0.67198 (7)	0.0509 (3)
S(4)	0.00763 (11)	0.71840 (9)	0.84761 (7)	0.0558 (4)
S(5)	0.42091 (12)	0.63566 (10)	0.83101 (8)	0.0628 (4)
S(6)	0.18074 (12)	0.96516 (10)	0.81993 (10)	0.0620 (4)
P(1)	0.27301 (10)	0.87404 (9)	0.52604 (7)	0.0437 (3)
P(2)	0.07759 (11)	0.52312 (9)	0.77900 (7)	0.0510 (4)
P(3)	0.32725 (14)	0.83550 (11)	0.89675 (8)	0.0674 (5)
C(1)	0.2726 (5)	1.0536 (4)	0.4968 (3)	0.056 (2)
C(2)	0.2393 (6)	1.1498 (5)	0.5842 (4)	0.077 (2)
C(3)	0.3049 (5)	0.7936 (4)	0.4056 (3)	0.060 (2)
C(4)	0.2883 (6)	0.6488 (5)	0.4090 (4)	0.077 (2)
C(5)	-0.0753 (5)	0.5102 (4)	0.7301 (4)	0.066 (2)
C(6)	-0.1089 (6)	0.6045 (6)	0.6438 (4)	0.083 (2)
C(7)	0.1146 (6)	0.3755 (4)	0.8643 (4)	0.071 (2)
C(8)	0.2468 (7)	0.3530 (4)	0.9095 (4)	0.091 (3)
C(9)	0.2151 (8)	0.8375 (7)	1.0247 (4)	0.102 (3)
C(10)	0.3025 (12)	0.7398 (10)	1.0910 (5)	0.154 (5)
C(11)	0.4758 (8)	0.9030 (6)	0.8996 (5)	0.097 (3)
C(12)	0.5570 (8)	0.9373 (8)	0.8017 (6)	0.115 (4)

0.116 (4) Å<sup>2</sup>.  $R = 0.032$ ,  $wR = 0.041$ ,  $S = 1.03$ ,  $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 0.60/-0.49$  Å<sup>-3</sup>,  $(\Delta/\sigma)_{\text{average}} = 0.07$  (8), 291 parameters. No extinction effects were detected. The rather large displacement factor for the terminal C(10)H<sub>3</sub> group indicates disorder, which could not be described by alternative positions in the refinement.

The data and the final model were compared by probability plotting (Abrahams & Keve, 1971) of ordered values of  $\delta R_i = \Delta F_i / \sigma(|F_o|_i)$  vs those expected for ordered normal deviates [ $\sigma(|F_o|_i) = w^{-1/2}$ ]. The result was a slope of 0.967 (2), an intercept of 0.06 (2) and a correlation coefficient of 0.9952. The slope and intercept of the  $\delta R$  plot and the related  $S$  value indicate that the systematic errors are small and the  $\sigma(|F_o|_i)$  is on average rather well estimated.

Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The system of computer programs used in this study is described by Lundgren (1982).

**Discussion.** Table 1 shows final fractional coordinates and equivalent isotropic displacement parameters for non-H atoms.\* The structure consists of discrete molecules of [Cr{S<sub>2</sub>P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}<sub>3</sub>] in which the Cr atom is coordinated by six S atoms in a distorted octahedral environment. In Fig. 1 the complex is viewed along the pseudo-threefold axis. Selected bond distances and

\* Lists of structure factors, anisotropic displacement factors and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44959 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* 1 BM (Bohr magneton) =  $9.274 \times 10^{-24}$  J T<sup>-1</sup>.

angles are shown in Table 2. The Cr—S distances range from 2.428 (1) to 2.451 (1), average 2.442 (8) Å.\* This is in agreement with the average distance of 2.425 (5) Å found in the related compound  $[\text{Cr}\{\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2\}_3]$  (Schousboe-Jensen & Hazell, 1972). The distortion from octahedral geometry may be described by the twist angle  $\varphi$  between opposite triangular faces of the octahedra along the pseudo-threefold axis (Stiefel & Brown, 1972). In an undistorted octahedron this angle is  $60^\circ$  and for a triangular prism it is  $0^\circ$ . In the title compound the three twist angles are  $47.44$  (5),  $47.82$  (5) and  $46.28$  (5), average  $47.2$  (8) $^\circ$ , indicating that the coordination polyhedron is almost octahedral. The similarity between the three angles clearly shows the almost perfect threefold axis, neglecting the ethyl groups. In  $[\text{Cr}\{\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2\}_3]$  the average twist angle is  $46.9$  (9) $^\circ$ .

The P—S bond distances are all equal, average 2.014 (8) Å, as is usually found in coordination compounds of this type. Thus the negative charge is delocalized over the two P—S bonds which have bond lengths intermediate between a single and a double bond (Wasson, Wolterman & Stoklasa, 1973). The P—C and C—C bond lengths are unexceptional, average 1.822 (7) and 1.495 (16) Å, respectively.

The ethyl groups have different conformations in the three ligands. Their appearance can be described by the torsion angle C—C—P—C (Table 2). In the nomenclature proposed by Klyne & Prelog (1960) this corresponds to two (*ap*, *ap*) and one (*sc*, *ap*) conformation† for the three ligands. This obviously breaks the threefold symmetry of the complex. The reason for this variation in conformation must be the packing of the complexes in the crystal. The structure is

\* Standard deviations of average values  $x$  are here and below estimated as  $[\sum(x-\bar{x})^2/(n-1)]^{1/2}$ .

† For *ap* (antiperiplanar) the torsion angle  $\tau$  is in the range  $\pm 180 \pm 30^\circ$ ; for *sc* (synclinal)  $\tau$  is  $\pm 60 \pm 30^\circ$ ; and for *ac* (anticlinal)  $\tau$  is  $\pm 120 \pm 30^\circ$ .

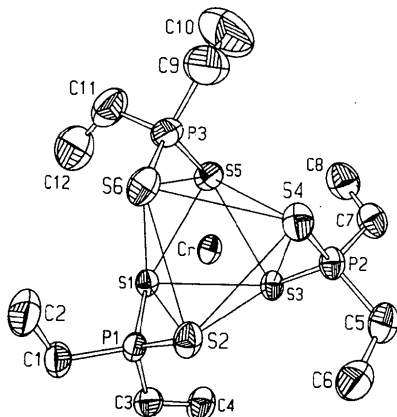


Fig. 1. Perspective view of the title compound with the atom-numbering scheme.

Table 2. Bond distances (Å), angles ( $^\circ$ ) and torsion angles ( $^\circ$ ) with e.s.d.'s in parentheses

Cr—S(1)	2.428 (1)	P(1)—C(1)	1.817 (3)
Cr—S(2)	2.437 (1)	P(1)—C(3)	1.817 (4)
Cr—S(3)	2.447 (1)	P(2)—C(5)	1.825 (4)
Cr—S(4)	2.447 (1)	P(2)—C(7)	1.819 (4)
Cr—S(5)	2.451 (1)	P(3)—C(9)	1.835 (6)
Cr—S(6)	2.441 (1)	P(3)—C(11)	1.817 (5)
P(1)—S(1)	2.017 (1)	C(1)—C(2)	1.495 (6)
P(1)—S(2)	2.020 (1)	C(3)—C(4)	1.517 (6)
P(2)—S(3)	2.013 (1)	C(5)—C(6)	1.505 (7)
P(2)—S(4)	2.020 (1)	C(7)—C(8)	1.498 (7)
P(3)—S(5)	2.017 (1)	C(9)—C(10)	1.470 (9)
P(3)—S(6)	1.998 (1)	C(11)—C(12)	1.484 (9)
S(1)—S(2)	3.198 (1)		
S(3)—S(4)	3.214 (1)		
S(5)—S(6)	3.227 (1)		
S(1)—Cr—S(2)	82.21 (3)	S(1)—P(1)—C(1)	112.38 (14)
S(3)—Cr—S(4)	82.11 (3)	S(2)—P(1)—C(3)	113.19 (15)
S(5)—Cr—S(6)	82.54 (4)	S(3)—P(2)—C(5)	112.47 (16)
S(1)—P(1)—S(2)	104.81 (5)	S(4)—P(2)—C(7)	112.13 (17)
S(3)—P(2)—S(4)	105.66 (5)	S(5)—P(3)—C(9)	111.78 (21)
S(5)—P(3)—S(6)	106.95 (6)	S(6)—P(3)—C(11)	110.72 (20)
C(1)—P(1)—C(3)	103.13 (19)	P(1)—C(1)—C(2)	115.18 (29)
C(5)—P(2)—C(7)	103.43 (21)	P(1)—C(3)—C(4)	114.57 (31)
C(9)—P(3)—C(11)	107.70 (32)	P(2)—C(5)—C(6)	114.38 (29)
		P(2)—C(7)—C(8)	114.73 (33)
		P(3)—C(9)—C(10)	115.57 (54)
		P(3)—C(11)—C(12)	115.13 (40)
C(1)—P(1)—C(3)—C(4)	-171.9 (3)	C(6)—C(5)—P(2)—C(7)	-169.8 (4)
C(2)—C(1)—P(1)—C(3)	176.7 (3)	C(9)—P(3)—C(11)—C(12)	-168.1 (5)
C(5)—P(2)—C(7)—C(8)	175.2 (4)	C(10)—C(9)—P(3)—C(11)	-64.4 (7)

stabilized by van der Waals forces only; the closest intermolecular contact involving the non-hydrogen atoms is  $3.74$  (1) Å [C(11)—C(11),  $1-x$ ,  $2-y$ ,  $2-z$ ].

Comparison of the title compound with  $[\text{Cr}\{\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2\}_3]$  (Schousboe-Jensen & Hazell, 1972) reveals that the replacement of the  $\text{OC}_2\text{H}_5$  groups with  $\text{C}_2\text{H}_5$  has no significant effect on the bond distances and angles in the  $\text{CrS}_6$  octahedra or in the deformation of the octahedra. However, the conformations of the  $\text{C}_2\text{H}_5$  and  $\text{OC}_2\text{H}_5$  groups are different, one being (*ap*, *ap*) and two (*ac*, *ac*) in  $[\text{Cr}\{\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2\}_3]$ .

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