complex) and 2·258 (2) Å (phosphine complex) show that although triphenylphosphite is a weaker σ-electron donor it is a much better π-electron acceptor than triphenylphosphine, resulting in a relatively strong Rh—P bond. The greater thermodynamic *trans* influence of the N atom, relative to that of the O atom of the chelate ring, is proved by the substitution of the carbonyl group *trans* to the N atom and is consistent with the summarized *trans* influence of different donor atoms (Graham, Lamprecht, Potgieter, Roodt & Leipoldt, 1990).

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Tris(dimethyldithiophosphinato)chromium(III) – Orthorhombic Form

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Abstract. $C_6H_{18}CrP_3S_6$, $M_r = 427{\cdot}51$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}107\ (1)$, $b = 9{\cdot}632\ (2)$, $c = 21{\cdot}530\ (2)$ Å, $V = 1888\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}50$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 14·6 cm^{-1}, $F(000) = 876$, T = 294 (1) K, $R = 0{\cdot}030$ for 3040 unique observed reflections of 4184 total data. The complex has trigonally distorted octahedral geometry [average trigonal twist 12·1 (3)°] similar to that observed for the monoclinic form. Cr—S 2·432 (4), P—S 2·010 (2) Å.

Experimental. The title compound was prepared by the method of Cavell, Byers & Day (1971) and crystallized from ethanol/CH_2Cl_2 to give two crystal forms – the known monoclinic modification (Buranda & Pinkerton, 1990) and a new orthorhombic form as dark blue rods.

Blue rod, 0·40 × 0·10 × 0·05 mm, mounted on a glass fiber, Enraf–Nonius CAD-4 diffractometer, graphite monochromator, θ–2θ scan technique, backgrounds obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974), unit-cell constants from the setting angles of 25 reflections in the range $10 < \theta < 14°$. Empirical absorption correction (from 0·858 to 0·999 on I), $2\theta_{\max} = 52{\cdot}0°$, $0 < h < 11$, $0 < k < 11$, $-26 < l < 26$; anisotropic decay (from 0·949 to 1·080 on I); reflection averaging $R_{\rm int} = 2{\cdot}3\%$, 4184 total reflections measured, 3717 nonsymmetry equivalent reflections, 3040 reflections with $F_o^2 > 3{\cdot}0\sigma(F_o^2)$. Solution by direct methods (*MULTAN*; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refinement by full-matrix least squares, function minimized was $\sum w(|F_o| - |F_c|)^2$, weight w is defined as $4F_o^2/\sigma^2(F_o^2)$, H atoms refined as riding atoms. 145 refined parameters, $R = 0{\cdot}030$, $wR = 0{\cdot}038$, $S = 1{\cdot}09$, largest shift $= 0{\cdot}03\sigma$, high peak in final difference map 0·37 (11) e Å^{-3}, low peak −0·24 (11) e Å^{-3}, enantiomorph confirmed by R factor test ($R = 0{\cdot}035$ for enantiomorph, bulk sample is racemic mixture of enantiomorphic crystals). Scattering factors for neutral atoms and the values for f' and f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV); computer programs *MolEN* (Fair, 1990).

Final atomic coordinates are reported in Table 1, bond lengths and angles in Table 2.* Fig. 1 prepared using *ORTEP* (Johnson, 1976).

Related literature. The structures of a number of tris(dithiophosphinato)chromium(III) complexes

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* Lists of structure factors, anisotropic thermal parameters, torsion angles, least-squares-planes data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54199 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters and their e.s.d.'s in parentheses*

	x	*y*	*z*	*B* (Å^2)
Cr	0·77658 (6)	0·95583 (6)	0·37094 (2)	3·14 (1)
S1	0·5701 (1)	0·82481 (9)	0·33179 (5)	3·80 (2)
S2	0·8462 (1)	0·7612 (1)	0·43639 (4)	4·85 (2)
S3	0·6204 (1)	1·0500 (1)	0·45292 (4)	3·88 (2)
S4	0·6988 (1)	1·12169 (9)	0·29174 (5)	3·74 (2)
S5	0·9620 (1)	0·8598 (1)	0·30252 (4)	4·34 (2)
S6	0·9519 (1)	1·1244 (1)	0·41184 (5)	4·41 (2)
P1	0·5288 (1)	0·99201 (9)	0·27839 (4)	3·40 (2)
P2	1·0016 (1)	0·7267 (1)	0·37221 (4)	3·75 (2)
P3	0·7909 (1)	1·1768 (1)	0·47132 (4)	3·46 (2)
C1	0·5162 (6)	0·9486 (4)	0·1976 (2)	6·2 (1)
C2	0·3549 (5)	1·0667 (5)	0·2994 (2)	5·2 (1)
C3	1·1795 (5)	0·7520 (6)	0·4045 (2)	6·4 (1)
C4	0·9979 (6)	0·5513 (4)	0·3449 (2)	6·0 (1)
C5	0·7478 (5)	1·3569 (4)	0·4633 (2)	5·0 (1)
C6	0·8418 (5)	1·1548 (5)	0·5510 (2)	5·2 (1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $8\pi^2/3$ trace *U*.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cr	S1	2·417 (1)	S4	P1	2·010 (2)
Cr	S2	2·429 (1)	S5	P2	2·006 (2)
Cr	S3	2·441 (1)	S6	P3	2·011 (2)
Cr	S4	2·442 (1)	P1	C1	1·793 (5)
Cr	S5	2·424 (1)	P1	C2	1·796 (5)
Cr	S6	2·441 (1)	P2	C3	1·781 (6)
S1	P1	2·014 (2)	P2	C4	1·790 (5)
S2	P2	2·006 (2)	P3	C5	1·787 (5)
S3	P3	2·015 (2)	P3	C6	1·790 (5)

S1	Cr	S2	90·14 (5)	Cr	S6	P3	85·41 (5)
S1	Cr	S3	89·58 (4)	S1	P1	S4	105·75 (7)
S1	Cr	S4	82·66 (4)	S1	P1	C1	112·3 (2)
S1	Cr	S5	97·51 (5)	S1	P1	C2	109·9 (2)
S1	Cr	S6	169·11 (5)	S4	P1	C1	109·4 (2)
S2	Cr	S3	91·10 (5)	S4	P1	C2	113·3 (2)
S2	Cr	S4	170·29 (5)	C1	P1	C2	106·3 (3)
S2	Cr	S5	82·90 (5)	S2	P2	S5	106·42 (7)
S2	Cr	S6	97·67 (5)	S2	P2	C3	110·5 (2)
S3	Cr	S4	95·32 (4)	S2	P2	C4	111·7 (2)
S3	Cr	S5	170·70 (5)	S5	P2	C3	111·6 (2)
S3	Cr	S6	82·72 (4)	S5	P2	C4	110·8 (2)
S4	Cr	S5	91·56 (4)	C3	P2	C4	105·9 (3)
S4	Cr	S6	90·37 (5)	S3	P3	S6	106·51 (7)
S5	Cr	S6	91·00 (5)	S3	P3	C5	113·6 (2)
Cr	S1	P1	85·81 (5)	S3	P3	C6	108·4 (2)
Cr	S2	P2	84·97 (6)	S6	P3	C5	110·0 (2)
Cr	S3	P3	85·33 (5)	S6	P3	C6	113·0 (2)
Cr	S4	P1	85·23 (5)	C5	P3	C6	105·4 (3)
Cr	S5	P2	85·09 (5)				

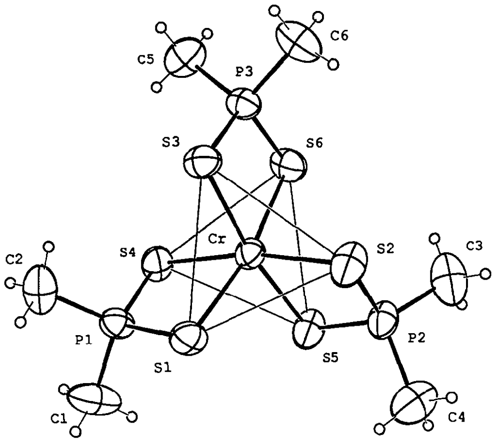

Fig. 1. Tris(dimethyldithiophosphinato)chromium(III) viewed down the non-crystallographic threefold axis.

have been reported (Schousboe-Jensen & Hazell, 1972; Svensson & Albertsson, 1988; Buranda & Pinkerton, 1990). All of these compounds contain the CrS_6 chromophore and the dithio ligands are all bidentate.

The present study concerns the orthorhombic modification of the title compound obtained from solution along with the previously reported monoclinic form (Buranda & Pinkerton, 1990). The crystals used in the previous study were obtained by sublimation.

The molecular structure reported here is essentially identical to that of the monoclinic form. Cr—S = 2·432 (4) [*vs* 2·435 (3) Å]; P—S = 2·010 (2) [*vs* 2·010 (2) Å]; bidentate angles subtended at chromium 82·76 (2) [*vs* 82·73 (6)°]; S—P—S = 106·2 (2) [*vs* 106·5 (3)°]; Cr—S—P = 85·3 (1) [*vs* 84·7 (3)°]. The main structural parameter of interest in these compounds is the trigonal distortion of the formally octahedral geometry due to the constraints imposed by the presence of bidentate ligands (Kepert, 1977). By measuring the torsion angle defined by one sulfur atom each from the upper and lower triangle (see Fig. 1) and the midpoints of these triangles, the average distortion from octahedral or, more correctly, trigonal antiprismatic geometry is 12·1 (3) *vs* 12 (1)° of trigonal twist for the monoclinic modification.

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