Crystallography (1974). A final difference synthesis showed no significant peaks. All programs used were from the XRAY system (1976). Table 1 gives the final positional parameters for non-hydrogen atoms. Table 2 shows some selected bond lengths and angles whilst Table 3 gives some information on the planarity of the molecule. Fig. 1 shows the numbering scheme.

Discussion. The product of the photocondensation of mer-[IrCl$_3$\{S(C$_2$H$_5$)$_2$\}$_3$] retains the octahedral coordination generally found for complexes of Ir^{III}. The structure of the isomer studied here, with two bridging Cl ligands and the diethyl sulphide groups *trans* to the bridging groups on one Ir atom, and *cis* on the other, is similar to that found for [Rh$_2$Cl$_6$\{P(n-C$_4$H$_9$)$_3$\}$_4$] (Muir *et al.*, 1974) and that proposed from NMR and chemical evidence for [Rh$_2$Cl$_6$\{S(CH$_3$)$_2$\}$_4$] (Anderson, Barnes, Goggin & Goodfellow, 1978).

The distortions from octahedral geometry are minor: the Ir atoms, the bridging and terminal Cl ligands (plane A) are coplanar within experimental error, but the bond angles at the bridging Cl atoms are greater than 90° with a corresponding reduction in bond angles at the Ir atoms. The ligands perpendicular to the bridging plane (plane C, Table 3) are coplanar with the Ir atoms, but the S(1) atoms bonded to Ir(1) are twisted out of the bridging plane, as shown by the large deviations for plane B and the low value (84·8°) of the angle Cl(1)—Ir(1)—S(1).

The bond lengths (Table 2) show a pronounced *trans* influence. If it is assumed that a bridging Cl is a weaker

ligand than a terminal Cl atom (Smith & Fryer, 1970), then the shortening of metal—ligand bond lengths on going from a position *cis* to the bridging plane [for Cl(1) and S(2)] to a position *trans* to the bridging groups [Cl(2) and S(1)] is understood. In accord with NQR data (Jones & Williams, 1977) the greater *trans* influence of the sulphide ligands is shown by the significantly greater Ir—Cl(3) distance when Cl(3) is *trans* to a sulphide.

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Structure of μ-Chloro-pentachloro-μ-(diethyl sulphide)-tris(diethyl sulphide)diiridium(III)

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Abstract. [Ir$_2$Cl$_6$\{S(C$_2$H$_5$)$_2$\}$_4$], C$_{16}$H$_{40}$Cl$_6$Ir$_2$S$_4$, monoclinic, $P2_1/c$, $a = 13\cdot692$ (6), $b = 12\cdot816$ (1), $c = 20\cdot695$ (2) Å, $\beta = 123\cdot66$ (4)°, $Z = 4$. The molecule consists of two octahedrally coordinated Ir atoms bridged by one Cl and one diethyl sulphide ligand. One Ir has a diethyl sulphide group *trans* to the bridging diethyl sulphide ligand, the other two mutually *trans* diethyl sulphide groups perpendicular to the plane of the Ir atoms and the bridging ligands. The structure was refined to $R(F) = 0\cdot032$ for 1316 independent reflections with $I > 3\sigma(I)$.

Introduction. The title compound is one of two isomers of composition [Ir$_2$Cl$_6$\{S(C$_2$H$_5$)$_2$\}$_4$] formed on photolysis of mer-[IrCl$_3$\{S(C$_2$H$_5$)$_2$\}$_3$] in benzene solution (Kauffman, Tsai, Gubelmann & Williams, 1980). The crystal structure determination was undertaken to

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confirm the suspected presence of a bridging diethyl sulphide group and to determine the exact stereochemistry of the product. The structure of the other isomer is given in the preceding paper (Williams, Flack & Vincent, 1980).

The orange tabular crystals were obtained by evaporation of dichloromethane–ethanol solutions. Oscillation and Weissenberg photographs showed the chosen crystal to be monoclinic and gave approximate values for the cell dimensions. Systematic absences were observed for $h0l$, l odd, and $0k0$, k odd, uniquely indicating space group $P2_1/c$.

Cell dimensions and intensities were obtained on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. 1316 independent reflections up to sin $\theta/\lambda = 0.481$ Å^{-1} were measured. 462 reflections with $I < 3\sigma(I)$ were ignored. Lorentz and polarization corrections were applied but no absorption correction was made [μ(Mo $K\alpha$) = 9.6 mm^{-1}].

A Patterson synthesis gave the positions of the Ir atoms, and successive difference syntheses the positions of the Cl, S and C atoms. It was not possible to locate the H atoms, even after refining all other atoms with anisotropic thermal parameters, and they were therefore added at positions calculated for

tetrahedral geometry at the C atoms ($d_{C-H} = 1.093$ Å, $U = 0.1$ Å^2). Final full-matrix least-squares refinement of all parameters other than those of the H atoms converged to $R = 0.032$ with 253 variables. Weights $w = 1/[\sigma(F_o)]^2$ were used and gave $R_w = 0.027$. The value of $[\sum_i w_i(\Delta F_i)^2/(m - n)]^{1/2}$ (m = number of measured reflections, n = number of variables) was 1.088.*

Scattering factors for neutral atoms were taken from Cromer & Mann (1968), and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). A final difference synthesis showed no significant peaks. All programs used were from the XRAY system (1976). Table 1 gives the final positional parameters for nonhydrogen atoms. Table 2 gives some selected bond lengths, Table 3 selected bond angles, and Table 4 least-squares-planes data. Fig. 1 shows the atom numbering.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35050 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic fractional coordinates and equivalent isotropic temperature factors* ($\times 10^2$) *for nonhydrogen atoms*

E.s.d.'s are given in parentheses.

	x	y	z	U (Å^2)
Ir(1)	0.39666 (7)	0.17581 (8)	0.09531 (4)	4.10 (5)
Ir(2)	0.15520 (7)	0.29822 (8)	−0.07297 (4)	4.41 (5)
Cl(1)	0.2674 (6)	0.0550 (5)	0.0934 (4)	7.3 (4)
Cl(2)	0.5262 (5)	0.2947 (5)	0.0942 (4)	6.2 (4)
Cl(3)	0.4897 (5)	0.1943 (6)	0.2286 (3)	7.4 (3)
Cl(4)	0.2976 (4)	0.1652 (5)	−0.0426 (3)	5.5 (3)
Cl(5)	0.0646 (5)	0.2761 (6)	−0.2074 (3)	7.7 (4)
Cl(6)	0.0201 (5)	0.4270 (6)	−0.0918 (4)	7.1 (4)
S(1)	0.5304 (5)	0.0493 (5)	0.1080 (4)	5.8 (4)
S(2)	0.2567 (4)	0.3066 (5)	0.0617 (3)	4.0 (3)
S(3)	0.2778 (5)	0.4287 (6)	−0.0731 (4)	6.5 (4)
S(4)	0.0272 (4)	0.1673 (6)	−0.0785 (3)	6.1 (3)
C(11)	0.676 (2)	0.080 (2)	0.195 (1)	7 (1)
C(12)	0.501 (2)	−0.082 (2)	0.133 (1)	9 (2)
C(13)	0.773 (2)	0.031 (2)	0.191 (1)	8 (2)
C(14)	0.409 (2)	−0.139 (2)	0.059 (2)	9 (2)
C(21)	0.152 (1)	0.285 (2)	0.091 (1)	5 (1)
C(22)	0.332 (2)	0.427 (2)	0.108 (1)	5 (1)
C(23)	0.209 (2)	0.291 (2)	0.179 (1)	8 (2)
C(24)	0.258 (2)	0.521 (2)	0.094 (2)	8 (2)
C(31)	0.184 (2)	0.528 (3)	−0.147 (1)	9 (2)
C(32)	0.339 (3)	0.361 (2)	−0.127 (2)	10 (2)
C(33)	0.184 (2)	0.637 (3)	−0.115 (2)	11 (2)
C(34)	0.427 (4)	0.418 (3)	−0.127 (3)	16 (4)
C(41)	0.040 (2)	0.051 (2)	−0.124 (2)	8 (2)
C(42)	−0.123 (2)	0.209 (2)	−0.156 (2)	9 (2)
C(43)	−0.015 (3)	−0.046 (2)	−0.116 (2)	10 (2)
C(44)	−0.198 (3)	0.207 (3)	−0.130 (2)	16 (3)

Table 2. *Selected bond lengths* (Å)

E.s.d.'s are given in parentheses.

Ir(1)–Cl(1)	2.335 (8)	Ir(2)–Cl(4)	2.397 (6)
Ir(1)–Cl(2)	2.349 (7)	Ir(2)–Cl(5)	2.352 (6)
Ir(1)–Cl(3)	2.322 (6)	Ir(2)–Cl(6)	2.345 (8)
Ir(1)–Cl(4)	2.390 (6)	Ir(2)–S(2)	2.327 (5)
Ir(1)–S(1)	2.349 (7)	Ir(2)–S(3)	2.370 (8)
Ir(1)–S(2)	2.343 (6)	Ir(2)–S(4)	2.383 (7)

Table 3. *Selected bond angles* (°)

E.s.d.'s are given in parentheses.

S(2)–Ir(1)–Cl(4)	81.7 (2)	C(11)–S(1)–C(12)	101.8 (10)
S(2)–Ir(2)–Cl(4)	81.9 (2)	C(21)–S(2)–C(22)	105.4 (12)
Ir(1)–S(2)–Ir(2)	99.8 (3)	C(31)–S(3)–C(32)	98.9 (14)
Ir(1)–Cl(4)–Ir(2)	96.5 (3)	C(41)–S(4)–C(42)	99.4 (12)

Table 4. *Least-squares planes: atoms defining the planes, and their distances from them* (Å)

E.s.d.'s of distances from the planes are 0.002 Å for Ir atoms and 0.015 Å for other atoms.

Plane A

Ir(1) −0.04, Ir(2) 0.02, S(2) 0.03, Cl(4) −0.02, S(1) 0.04, Cl(3) −0.01, Cl(5) −0.01, Cl(6) 0.00

Plane B

Ir(1) 0.02, Ir(2) 0.02, Cl(1) 0.07, Cl(2) −0.09, S(3) 0.07, S(4) −0.09

Angle between planes A and B = 88.6 (5)°

Discussion. The structure is basically that of two edge-sharing octahedra as found for the other isomer, but with a diethyl sulphide replacing a bridging Cl ligand. The coordination of the Ir atoms is close to regular octahedral with the greatest distortion due, as in the other isomer, to the acute angles between the two Ir-bridging ligand bonds [81·7 for Ir(1) and 81·9° for Ir(2)]. The angles between two *cis* ligand–metal bonds where neither ligand is bridging are all close to 90°, but vary considerably more for Ir(1) (between 84·4 and 94·6°) than for Ir(2) (between 88·1 and 92·2°). This is slightly surprising as Ir(2) with three bulky diethyl sulphide ligands would normally be expected to show a greater distortion due to ligand–ligand interactions. The ligating atoms all lie close either to a plane (*A*) passing through the Ir atoms and the bridging ligands, or to a plane (*B*) passing through the Ir atoms and perpendicular to *A* (Table 4).

Only one other structural determination involving a bridging diethyl sulphide group is known to the authors. In this work (Sales, Stokes & Woodward, 1968) the authors compared the structures of [Pd₂Br₄- {S(CH₃)₂}₂] (bromine bridged) and [Pt₂Br₄- {S(C₂H₅)₂}₂] (diethyl sulphide bridged) and found that the *M*–S distances decreased in the case of a bridging sulphide group. This is not the case for the compound discussed here, where the S(2)–Ir distance is shorter than that for a sulphide group *trans* to another sulphide but longer than that found in the preceding paper for a diethyl sulphide group *trans* to a bridging Cl [2·301 (5) Å]. We find, in agreement with previous results, that the C–S–S angle of diethyl sulphide is significantly greater when the ligand is bridging than when it is unidentate. This would imply a greater participation of the sulphur 3s orbital in bonding, to be expected if the S atom is using both lone pairs for complexation.

The low symmetry of the molecule limits discussion of *cis* and *trans* influences, but we may note that the Ir–S(2) length is shorter when *trans* to a Cl than when *trans* to a diethyl sulphide. The *trans* influence of a ligand appears to fall on its becoming bridging. The Ir(1)–S(1) distance is significantly longer than that for a diethyl sulphide group *trans* to a bridging Cl, but less than that when *trans* to a unidentate diethyl sulphide. In comparison with the other isomer (Williams, Flack & Vincent, 1980) there is slight evidence for a *cis* effect shown by an increase in the Ir(2)–S(3) and Ir(2)–S(4) lengths on exchanging a bridging Cl for a bridging diethyl sulphide, but this is at the limit of experimental error.
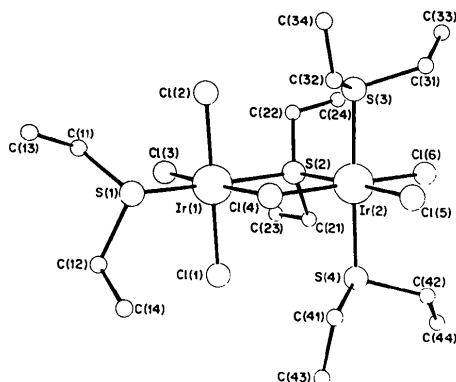

Fig. 1. View of the molecule showing the numbering system.

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