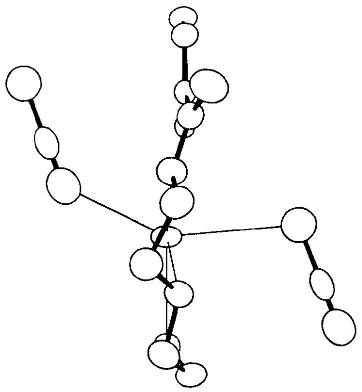

Fig. 2. *ORTEP* (Johnson, 1965) drawing of a molecule rotated 90° clockwise [around the O(10)—N(1) vector] from the view in Fig. 1.

The authors are grateful to R. Neustadt and F. W. Cagle for their assistance with the data collection. The data were collected while N. K. Dalley was on leave at The University of Utah. The diffractometer was purchased with funds provided by NSF Grant GU 3866. The interest of R. M. Izatt and J. S. Bradshaw was also appreciated. This work was supported in part by the US Public Health Service NIH Grant GM 18811.

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Acta Cryst. (1980). B**36**, 1204–1206

Structure of Di-μ-chloro-tetrachlorotetrakis(diethyl sulphide)diiridium(III)

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(*Received* 21 *December* 1979; *accepted* 22 *January* 1980)

Abstract. $[Ir_2Cl_6\{S(C_2H_5)_2\}_4]$, $C_{16}H_{40}Cl_6Ir_2S_4$, monoclinic, $C2/c$, $a = 18{\cdot}884\,(1)$, $b = 12{\cdot}700\,(1)$, $c = 14{\cdot}436\,(7)$ Å, $\beta = 118{\cdot}25\,(1)°$, $Z = 4$. The symmetry of the molecule is 2 with the Ir atoms on the twofold axis. Two Cl atoms bridge the Ir atoms which are octahedrally coordinated. One Ir has two mutually *cis* diethyl sulphide ligands in the plane of the bridging Cl atoms and the other two mutually *trans* diethyl sulphide groups perpendicular to the bridging Cl-atom plane. The structure was refined to $R(F) = 0{\cdot}029$ for 975 independent reflections with $I > 3\sigma(I)$.

Introduction. The title compound is one of two isomers of composition $[Ir_2Cl_6\{S(C_2H_5)_2\}_4]$ obtained on photolysis of *mer*-$[IrCl_3\{S(C_2H_5)_2\}_3]$ in benzene solution (Kauffman, Tsai, Gubelmann & Williams, 1980). Given the current interest in the photochemistry of coordination compounds, and the lack of any

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0567-7408/80/051204-03$01.00

structural data on the numerous dimeric complexes of Ir^{III}, a crystal structure determination was undertaken.

The red tabular crystals were obtained by evaporation of dichloromethane–ethanol solutions. Oscillation and Weissenberg photographs showed the crystal to be monoclinic and gave approximate values for the cell dimensions. Systematic absences were observed for hkl, $h + k = 2n + 1$ and $h0l$, h or l odd, identifying the space group as either Cc or $C2/c$. The compound is soluble in halogenated solvents, but it was possible to show that the density is $<2{\cdot}48$ Mg m^{-3}, implying $Z = 4$ ($d_c = 2{\cdot}086$ Mg m^{-3}). For $C2/c$ symmetry this requires the Ir atoms to be in special positions, as was found for the Rh atoms in $[Rh_2Cl_6\{P(C_4H_9)_3\}_4]$ (Muir, Muir & Rivera, 1974).

Cell dimensions and intensities were obtained on a Philips PW 1100 four-circle diffractometer with Mo $K\alpha$ radiation. 975 independent reflections up to $\sin\theta/\lambda = 0{\cdot}481$ Å^{-1} were measured. 179 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 showed the Ir atoms to be on the twofold axis and confirmed the space group as $C2/c$. The Cl and S atoms could also be located from the Patterson map, and the C atoms by a difference synthesis. 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 ($d_{C-H} = 1{\cdot}093$ Å, $U = 0{\cdot}1$ Å^2). Final full-matrix least-squares refinement of all parameters other than those of the H atoms converged to $R = 0{\cdot}029$ with 128 variables. Weights $w = 1/[\sigma(F_o)]^2$ were used and gave $R_w = 0{\cdot}027$. 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 1·713.*

Scattering factors for neutral atoms were taken from Cromer & Mann (1968), and anomalous-dispersion corrections from *International Tables for X-ray*

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

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

	x	y	z	U (Å^2)
Ir(1)	0	0·01640 (7)	0·25	5·11 (6)
Ir(2)	0	0·30048 (7)	0·25	5·95 (6)
Cl(1)	0·1118 (3)	0·0189 (4)	0·2193 (4)	7·5 (3)
Cl(2)	0·0640 (3)	0·4268 (4)	0·3811 (4)	10·3 (3)
Cl(3)	0·0557 (2)	0·1594 (4)	0·3732 (3)	5·9 (2)
S(1)	0·0689 (3)	−0·1145 (4)	0·3690 (4)	8·1 (3)
S(2)	0·1115 (3)	0·3007 (4)	0·2178 (4)	7·4 (3)
C(11)	0·160 (1)	−0·049 (1)	0·488 (1)	11 (1)
C(12)	0·018 (2)	−0·166 (2)	0·436 (2)	15 (2)
C(13)	0·219 (1)	−0·125 (2)	0·552 (2)	15 (2)
C(14)	−0·015 (1)	−0·273 (2)	0·395 (2)	16 (2)
C(21)	0·205 (1)	0·276 (2)	0·349 (1)	12 (1)
C(22)	0·131 (1)	0·435 (2)	0·194 (2)	13 (2)
C(23)	0·278 (1)	0·260 (2)	0·344 (2)	12 (1)
C(24)	0·169 (2)	0·445 (2)	0·129 (2)	16 (2)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Ir(1)–S(1)	2·301 (5)	Ir(2)–S(2)	2·363 (7)
Ir(1)–Cl(1)	2·353 (6)	Ir(2)–Cl(2)	2·335 (5)
Ir(1)–Cl(3)	2·408 (5)	Ir(2)–Cl(3)	2·390 (5)
Cl(1)–Ir(1)–S(1)	84·8 (2)	S(2)–Ir(2)–Cl(2)	90·4 (2)
Cl(1)–Ir(1)–Cl(3)	90·7 (2)	S(2)–Ir(2)–Cl(3)	88·5 (2)
Cl(3)–Ir(1)–Cl(3)	82·1 (2)	Cl(2)–Ir(2)–Cl(3)	92·0 (2)
Cl(3)–Ir(1)–S(1)	95·7 (2)	Cl(3)–Ir(2)–Cl(3)	82·8 (2)
Ir(1)–Cl(3)–Ir(2)	97·5 (1)		

Table 3. *Least-squares planes: atoms defining the planes, and their distances from them* (Å)

E.s.d.'s of distances from the plane are 0·015 Å.

Plane	
A	Ir(1) 0·02, Cl(3) −0·02, Ir(2) 0·02, Cl(2) −0·02
B	S(1) 0·08, Ir(1) −0·04, Cl(3) −0·12, Ir(2) 0·04, Cl(2) 0·03
C	Ir(1) −0·005, Ir(2) 0·005, Cl(1) 0·005, S(2) −0·005

Angles between planes (°)

$A \wedge C$	88·8 (5)	$B \wedge C$	87·6 (5)

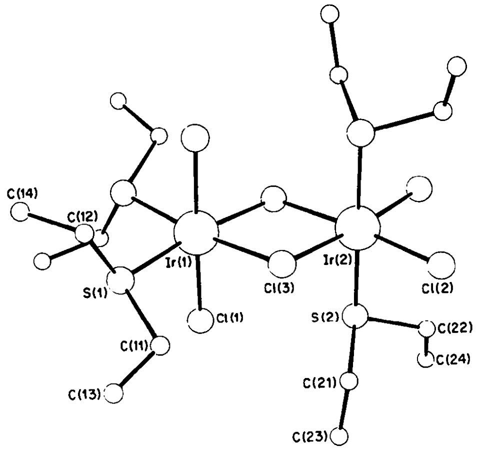

Fig. 1. View of the molecule showing the numbering system. Unnumbered atoms are related to numbered atoms by a horizontal twofold symmetry axis passing through the Ir atoms.

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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 35049 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*-$[\mathrm{IrCl_3\{S(C_2H_5)_2\}_3}]$ retains the octahedral coordination generally found for complexes of $\mathrm{Ir^{III}}$. 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 $[\mathrm{Rh_2Cl_6\{P(\mathit{n}\text{-}C_4H_9)_3\}_4}]$ (Muir *et al.*, 1974) and that proposed from NMR and chemical evidence for $[\mathrm{Rh_2Cl_6\{S(CH_3)_2\}_4}]$ (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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Acta Cryst. (1980). B**36**, 1206–1208

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

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(*Received* 21 *December* 1979; *accepted* 22 *January* 1980)

Abstract. $[\mathrm{Ir_2Cl_6\{S(C_2H_5)_2\}_4}]$, $\mathrm{C_{16}H_{40}Cl_6Ir_2S_4}$, monoclinic, $P2_1/c$, $a = 13{\cdot}692\,(6)$, $b = 12{\cdot}816\,(1)$, $c = 20{\cdot}695\,(2)$ Å, $\beta = 123{\cdot}66\,(4)°$, $Z = 4$. 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 $R(F) = 0{\cdot}032$ for 1316 independent reflections with $I > 3\sigma(I)$.

Introduction. The title compound is one of two isomers of composition $[\mathrm{Ir_2Cl_6\{S(C_2H_5)_2\}_4}]$ formed on photolysis of *mer*-$[\mathrm{IrCl_3\{S(C_2H_5)_2\}_3}]$ in benzene solution (Kauffman, Tsai, Gubelmann & Williams, 1980). The crystal structure determination was undertaken to

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0567-7408/80/051206-03$01.00