cite, $H_2Mn_7Si_3O_{14}$, $Mn-O_{av}=2\cdot22$ Å (Moore, 1970). Similarly $O-O_{av}$ for the oxygens associated with M(1) in senaite, 3·15 Å, compares closely with an $O-O_{av}=$ 3·12 Å in leucophoenicite. The coordination around the Mn atom in senaite is almost perfect octahedral, with six equivalent Mn–O distances, and with a variation in the O–Mn–O angles from 87·4 to 92·6°.

The mean M–O distance for the tetrahedrally coordinated metal atom M(2) is 2·00 Å. This value is very close to the sum of the ionic radii for tetrahedrally coordinated Fe^{2+} and O^{2-}, i.e. 2·01 Å (Shannon & Prewitt, 1969) and agrees with the value of 2·00 Å found for $(Fe^{2+}-O)_{tet}$ in titanomagnetite (Stout & Bayliss, 1975). The coordination polyhedron around M(2) is very regular with angles O–M(2)–O in the narrow range 107·0 to 111·7° and with apical and basal M(2)–O distances equal within experimental error. The three largest metal ions, Pb^{2+}, Mn^{2+}, and Fe^{2+}, are all ordered into sites on the trigonal axis (Fig. 4), and all have very regular coordination polyhedra. On the other hand, the largest distortions in the structure are associated with the smallest cations, Ti^{4+}, in the M(4) and M(5) sites. The distortion of the M(5)–O_6 octahedron is much greater than that for the M(4)–O_6 octahedron; the degree of distortion is related to the type and symmetry of the articulated polyhedra. Thus M(4)–O_6 shares edges with three other octahedra and corners with four octahedra and one tetrahedron and has $\Delta M-O=0\cdot13$ Å and $\Delta O-M-O=17\cdot51°$. The M(5)–O_6 octahedron shares edges with four octahedra and corners with four octahedra and two tetrahedra. Its range of metal–oxygen distances and oxygen–metal–oxygen angles is 0·27 Å and 26·44° respectively.

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The Crystal and Molecular Structure of μ-Chloro-di-μ-phenylthio-di[hydridobis(triphenylphosphine)iridium(III)] Perchlorate

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μ-Chloro-di-μ-phenylthio-di[hydridobis(triphenylphosphine)iridium(III)] perchlorate crystallizes with three molecules of acetone in space group $P2_1$ with $a=15\cdot013$ (3), $b=12\cdot918$ (1), $c=22\cdot044$ (4) Å, $\beta=91\cdot94$ (1)°, $Z=2$. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares calculations to final values of R and R_w of 0·050 and 0·070 for 7564 observed reflexions. The molecule contains two Ir atoms bridged by a Cl [Ir–Cl$=2\cdot558$ (2) Å] and by the S atoms of two phenylthiol ligands [mean Ir–S$=2\cdot407$ (7) Å]. The remaining three sites on each approximately octahedrally coordinated Ir atom are filled by two triphenylphosphine groups [mean Ir–P$=2\cdot329$ (3) Å] and a hydride.

Introduction

The dimeric iridium(III) hydride complex [IrHCl(SPh) (PPh$_3$)$_2$]$_2$ (1) (Herdé & Senoff, 1973) reacts with chloroform or dichloroethane to form an off-white powder (2) whose structure could not be elucidated by standard chemical techniques. Reaction of (1) with AgClO$_4$ in acetone under reflux, followed by

the removal of AgCl yielded a yellow solution from which a crystalline material (3) could be obtained. In order to elucidate the structure of (2) an X-ray analysis of (3) was carried out, and we report here the results.

Experimental

The crystals are yellow plates of irregular hexagonal cross-section elongated along **b**. The crystal used in the analysis had dimensions $0.19 \times 0.26 \times 0.56$ mm.

Unit-cell and space-group data were obtained by photographic and diffractometer methods, the lattice parameters being determined by least-squares treatment of the θ values for 12 reflexions measured with Mo $K\alpha$ radiation on the diffractometer.

Crystal data

$[C_{84}H_{72}ClIr_2P_4S_2]^+[ClO_4]^-.3C_3H_6O$. F.W. 1963·1, monoclinic, $a = 15.013$ (3), $b = 12.918$ (1), $c = 22.044$ (4) Å, $\beta = 91.94$ (1)°, $V = 4272.7$ Å³, $Z = 2$, $D_x = 1.53$, $D_m =$

Table 1. *Final fractional coordinates ($\times 10^5$ for iridium, 10^4 others) and isotropic temperature factors ($\times 10^3$) with e.s.d.'s in parentheses*

	x	y	z	U		x	y	z
Ir(1)	21380 (5)	25000	32930 (4)		C(136)	−446	4545	3763
Ir(2)	28080 (5)	30123 (9)	18771 (4)		C(131)	20	3684	3602
Cl(1)	1366 (4)	2219 (4)	2255 (2)		C(212)	3138	945	4600
Cl(2)	2764 (6)	2197 (9)	7423 (4)		C(213)	3546	601	5146
S(1)	3316 (3)	1869 (4)	2674 (3)		C(214)	3171	−255	5450
S(2)	2474 (3)	4054 (4)	2751 (2)		C(215)	2389	−769	5208
P(1)	1169 (3)	3454 (5)	3874 (2)		C(216)	1982	−426	4662
P(2)	1839 (4)	832 (4)	3634 (3)		C(211)	2357	431	4358
P(3)	2072 (4)	4157 (5)	1213 (3)		C(222)	2938	−869	3342
P(4)	3380 (4)	1862 (5)	1176 (3)		C(223)	3283	−1665	2975
					C(224)	2949	−1766	2392
O(1)	3578 (17)	2511 (23)	7702 (12)	175 (8)	C(225)	2269	−1072	2175
O(2)	2980 (15)	1426 (24)	6895 (12)	152 (8)	C(226)	1924	−275	2542
O(3)	2407 (16)	3263 (25)	7208 (13)	206 (9)	C(221)	2258	−174	3126
O(4)	2163 (19)	1852 (30)	7909 (15)	237 (10)	C(232)	268	785	4256
O(5)	3802 (18)	3422 (26)	5093 (14)	209 (10)	C(233)	−623	622	4351
O(6)	7497 (19)	3147 (28)	1250 (16)	247 (10)	C(234)	−1119	121	3909
O(7)	8840 (19)	460 (27)	900 (15)	242 (10)	C(235)	−723	−219	3371
C(1)	5206 (22)	2914 (32)	5387 (16)	142 (11)	C(236)	168	−56	3276
C(2)	4442 (25)	3437 (32)	5531 (18)	143 (12)	C(231)	664	445	3718
C(3)	4211 (28)	3653 (42)	6148 (20)	196 (15)	C(312)	464	3158	836
C(4)	6458 (25)	4538 (35)	1468 (18)	189 (13)	C(313)	−86	2542	463
C(5)	7268 (27)	4187 (37)	1285 (26)	163 (13)	C(314)	264	2219	−100
C(6)	8074 (24)	4832 (33)	1257 (17)	143 (11)	C(315)	1164	2511	−290
C(7)	8942 (27)	1015 (39)	1822 (20)	218 (14)	C(316)	1714	3127	83
C(8)	8737 (25)	128 (36)	1522 (20)	186 (13)	C(311)	1364	3450	646
C(9)	9514 (25)	−685 (36)	1715 (19)	177 (13)	C(322)	2432	5458	256
					C(323)	2924	6177	−62
C(12)	4936	2944	2770		C(324)	3712	6510	165
C(13)	5855	3082	3012		C(325)	4008	6124	711
C(14)	6181	2459	3466		C(326)	3516	5404	1030
C(15)	5588	1696	3678		C(321)	2728	5071	802
C(16)	4669	1558	3435		C(332)	686	4764	1933
C(11)	4344	2182	2982		C(333)	79	5462	2175
C(22)	3836	5485	2659		C(334)	125	6509	2051
C(23)	4622	6023	2848		C(335)	779	6858	1686
C(24)	5042	5733	3408		C(336)	1386	6160	1444
C(25)	4676	4904	3778		C(331)	1340	5113	1568
C(26)	3890	4366	3589 ·		C(412)	1774	791	939
C(21)	3470	4657	3029		C(413)	1249	−56	718
C(112)	1452	5561	3560		C(414)	1656	−912	471
C(113)	1804	6512	3633		C(415)	2588	−922	444
C(114)	2338	6705	4134		C(416)	3113	−76	665
C(115)	2522	5948	4561		C(411)	2706	781	913
C(116)	2171	4996	4488		C(422)	5133	1627	1387
C(111)	1636	4803	3987		C(423)	5878	1101	1671
C(122)	107	3023	4877		C(424)	5842	216	2045
C(123)	3	2687	5488		C(425)	5060	−142	2136
C(124)	771	2365	5867		C(426)	4315	383	1852
C(125)	1643	2378	5635		C(421)	4351	1268	1478
C(126)	1747	2713	5024		C(432)	3480	1980	−100
C(121)	979	3036	4646		C(433)	3772	2479	−640
C(132)	−372	2961	3194		C(434)	4288	3380	−611
C(133)	−1230	3098	2947		C(435)	4513	3782	−43
C(134)	−1696	3960	3108		C(436)	4222	3283	496
C(135)	−1304	4683	3516		C(431)	3705	2382	467

1·55 g cm^{-3}, μ(Mo $K\alpha$)=35·3 cm^{-1}, $F(000)$=1968, λ(Mo $K\alpha$)=0·7107 Å, space group $P2_1$ (C_2^2, No. 4).

Intensities were measured on a Hilger and Watts Y-290 four-circle diffractometer with the $\theta/2\theta$ step-scan technique and graphite monochromated Mo $K\alpha$ radiation. 70 steps, each of range 0·01° (θ) and of 1 s duration were taken through each diffracting position. Background counts of 35 s were measured at the start and end positions of each scan. The standard deviation of an intensity was calculated from $\sigma^2(I)=S+B+(dS)^2$, where S is the scan count, B the sum of the two background counts and d an empirical constant to allow for unknown experimental errors, taken as 0·05. Of 8124 reflexions with θ(Mo $K\alpha$)$\leq 25°$ (minimum interplanar spacing=0·84 Å), 352 had $I/\sigma(I)\leq 3\cdot0$ and were excluded from subsequent calculations. Averaging of equivalent reflexions produced an R of 0·02 and resulted in 7564 independent observed intensities. Lorentz and polarization factors were applied but absorption corrections were not. The maximum error as a result of this decision is less than 10% except at $\chi=90°$. The large number of data and hence the exorbitant cost of the calculation of transmission coefficients led to our decision to ignore absorption effects and also to carry out the refinement with only those 3726 reflexions with $\sin\theta\leq0\cdot33$. The structure was solved by a combination of Patterson and Fourier techniques with an initial phasing model consisting of the two Ir atoms. Isotropic least-squares refinement of the Ir, S, P and Cl atoms with the remaining atoms included as fixed contributors yielded R and R_w* values of 0·097 and 0·160 respectively. Scattering factors were those of Cromer & Mann (1968) and included corrections for the anomalous scattering of Ir (Cromer & Liberman, 1970). To simplify and reduce the size of the calculation, the phenyl rings were refined by a procedure (Sheldrick, 1976) in which each ring was required to remain centrosymmetric and planar. As well as this, one overall U was assigned for all 14 ring atoms bonded directly to a P or S, another for the 28 ring atoms *ortho* to these, a third for the 28 atoms *meta* to the first group and finally a fourth for the 14 *para* atoms. This was considered a reasonable approach since the thermal motion of phenyl C atoms is greatest for those most remote from the 'pivot' atom. These four thermal parameters were allowed to refine freely and acquired the final values 0·051, 0·062, 0·081 and 0·085 respectively. The final stage in the refinement was to allow the Ir, Cl, S and P atoms to assume anisotropic thermal parameters. Final values of R and R_w were 0·047 and 0·071 for the 3726 reflexions with $\sin\theta<0\cdot33$ and 0·050 and 0·070 respectively for all 7564 independent observed reflexions. Final values for the coordinates and anisotropic temperature factors are presented in Tables 1 and 2 respectively, with their standard deviations calculated from the inverse matrix

* $R_w=[\sum w|F_o-F_c|^2/\sum wF_o^2]^{1/2}$.

of the final refinement cycle.* The intensities of 15 Friedel pairs of reflexions were measured to establish that the anomalous dispersion of Ir in the polar space group $P2_1$ had been correctly handled. Bond lengths and valency angles are given in Tables 3 and 4 respectively. Standard deviations in these parameters are estimated from the full covariance matrix.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31454 (38 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Anisotropic temperature factors* (U's × 10^4 *for iridium*, 10^3 *others*)

Coefficients in the temperature factor expression:

$$\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^* +2U_{13}hla^*c^*+2U_{23}klb^*c^*)].$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir(1)	299 (5)	253 (5)	291 (5)	29 (4)	67 (4)	−26 (4)
Ir(2)	362 (6)	291 (6)	279 (5)	12 (4)	82 (4)	−31 (4)
Cl(1)	46 (3)	37 (4)	32 (3)	3 (3)	0 (3)	−7 (3)
Cl(2)	81 (5)	139 (9)	99 (6)	13 (7)	0 (5)	0 (6)
S(1)	35 (3)	25 (3)	38 (3)	−1 (3)	7 (3)	0 (3)
S(2)	35 (3)	24 (3)	33 (3)	0 (3)	12 (2)	−3 (3)
P(1)	34 (3)	29 (3)	37 (3)	2 (3)	9 (3)	−2 (3)
P(2)	43 (3)	20 (3)	42 (4)	5 (3)	7 (3)	−3 (3)
P(3)	42 (3)	41 (4)	38 (4)	4 (3)	7 (3)	0 (3)
P(4)	51 (4)	41 (4)	35 (4)	−6 (3)	11 (3)	−4 (3)

Table 3. *Bond lengths* (Å) *with their e.s.d.'s in parentheses*

Ir(1)–Cl(1)	2·556 (4)		Ir(2)–Cl(1)	2·559 (5)
Ir(1)–S(1)	2·412 (5)		Ir(2)–S(1)	2·400 (5)
Ir(1)–S(2)	2·399 (5)		Ir(2)–S(2)	2·416 (5)
Ir(1)–P(1)	2·324 (5)		Ir(2)–P(3)	2·332 (5)
Ir(1)–P(2)	2·330 (5)		Ir(2)–P(4)	2·329 (6)
Cl(2)–O(1)	1·41 (2)			
Cl(2)–O(2)	1·57 (2)			
Cl(2)–O(3)	1·55 (3)			
Cl(2)–O(4)	1·49 (3)			
S(1)—C(11)	1·712		S(2)—C(21)	1·776
P(1)—C(111)	1·892		P(3)—C(311)	1·854
P(1)—C(121)	1·817		P(3)—C(321)	1·802
P(1)—C(131)	1·830		P(3)—C(331)	1·845
P(2)—C(211)	1·826		P(4)—C(411)	1·808
P(2)—C(221)	1·841		P(4)—C(421)	1·759
P(2)—C(231)	1·849		P(4)—C(431)	1·783

Table 4. *Valency angles* (°) *with their standard deviations in parentheses*

Cl(1)–Ir(1)–S(1)	76·4 (2)		Cl(1)–Ir(2)–S(1)	76·5 (1)
Cl(1)–Ir(1)–S(2)	76·6 (1)		Cl(1)–Ir(2)–S(2)	76·3 (1)
Cl(1)–Ir(1)–P(1)	107·2 (2)		Cl(1)–Ir(2)–P(3)	94·0 (2)
Cl(1)–Ir(1)–P(2)	94·1 (2)		Cl(1)–Ir(2)–P(4)	107·2 (2)
S(1)—Ir(1)–S(2)	80·2 (2)		S(1)—Ir(2)–S(2)	80·1 (2)
S(1)—Ir(1)–P(1)	167·3 (2)		S(1)—Ir(2)–P(3)	169·0 (2)
S(1)—Ir(1)–P(2)	91·3 (2)		S(1)—Ir(2)–P(4)	88·7 (2)
S(2)—Ir(1)–P(1)	88·7 (2)		S(2)—Ir(2)–P(3)	92·3 (2)
S(2)—Ir(1)–P(2)	168·7 (2)		S(2)—Ir(2)–P(4)	167·3 (2)
P(1)—Ir(1)–P(2)	100·5 (2)		P(3)—Ir(2)–P(4)	99·5 (2)

Discussion

The analysis establishes the structure of (3) to be the triply bridged dimeric Ir^{III} complex shown schematically in Fig. 1 and in a stereo view in Fig. 2. To our knowledge, this is the first such compound reported.

From a correlation of spectroscopic evidence it can be concluded that (2) must be the chloride of the same cation.

The structure of the cation is most easily visualized as two octahedra sharing a face. The coordination sites at the apices of this face are occupied by a Cl and the two S atoms of the phenylthiol ligands. Each Ir is bonded to triphenylphosphine groups, trans to each S atom. The H atoms trans to the Cl were not located in this study but their presence is indicated by Ir–H spectroscopic evidence (Roberts, Ferguson & Senoff, 1975).

Individual Ir–S, Ir–Cl and Ir–P lengths do not differ significantly from the mean values for each bond type. The mean Ir–P length is 2·329 (r.m.s.d. = 0·003) Å, comparable with the known range of values 2·290–

in the valency angles: S(2)–Ir(1)–P(1) and S(1)–Ir(2)–P(4) are both 88·7 (2)° while S(1)–Ir(1)–P(2) and S(2)–Ir(2)–P(3) are 91·3 (2) and 92·3 (2)° respectively. Other more extreme deviations of Ir valence angles from the octahedral value of 90° occur between the

Table 5. *Equations of mean planes in the form* $Ax + By + Cz = D$ *where* x, y *and* z *are fractional coordinates referred to the unit-cell axes* a, b, *and* c

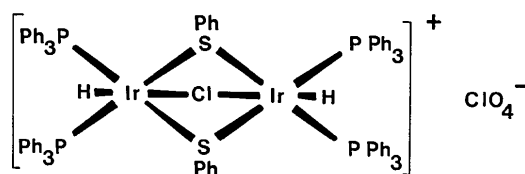|	A	B	C	D
Ir(1), S(1), S(2)	9·7721	3·2263	15·3085	7·9369
Ir(2), S(1), S(2)	13·6823	5·3114	−1·1020	5·2351

Fig. 1. Schematic representation of the μ-chloro-di-μ-phenyl-thio-di[hydridobis(triphenylphosphine)iridium(III)] cation.
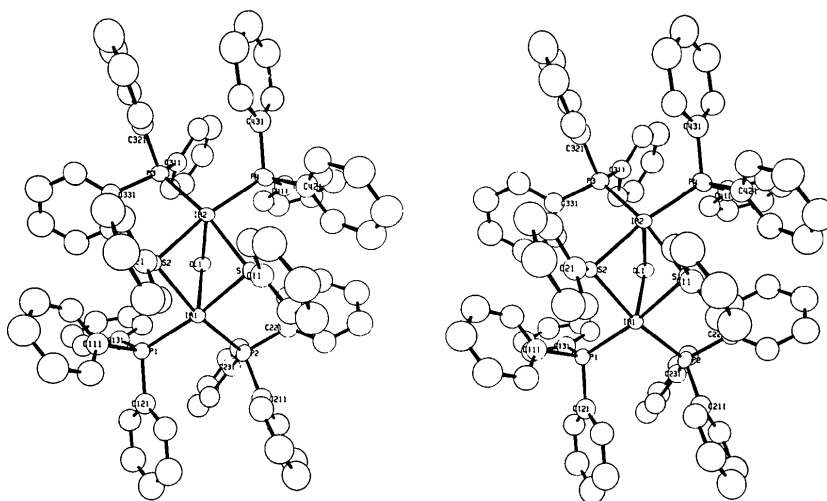

Fig. 2. Stereoscopic view of the cation.

2·382 Å (Albano, Bellon & Sansoni, 1971; Callahan, Strouse, Layton & Hawthorne, 1973; La Placa & Ibers, 1966). Bridging thiol ligands have also been observed in dicarbonylbis(triphenylphosphine)tris(toluene-3,4-dithiolato)diiridium(III)·(Khare & Eisenberg, 1972). Bridging Ir–S bonds in that compound are of two types averaging 2·47 and 2·38 Å. In the present structure we observe Ir–S lengths ranging from 2·399 to 2·416 [mean = 2·407 (7)] Å.

The molecule could conceivably show *mm* symmetry but in fact it achieves only twofold symmetry as a result of the twisting of pairs of triphenylphosphine ligands out of the two IrS_2 planes (Table 5) as shown in Fig. 3. This reduction in symmetry is also manifested
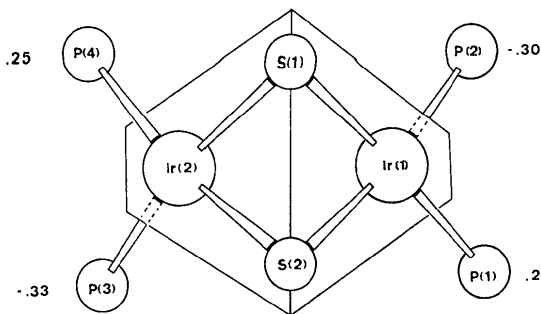

Fig. 3. The twisting of pairs of triphenylphosphine ligands out of the two IrS_2 planes (see Table 5) and the distances (Å) of the P atoms from these planes.
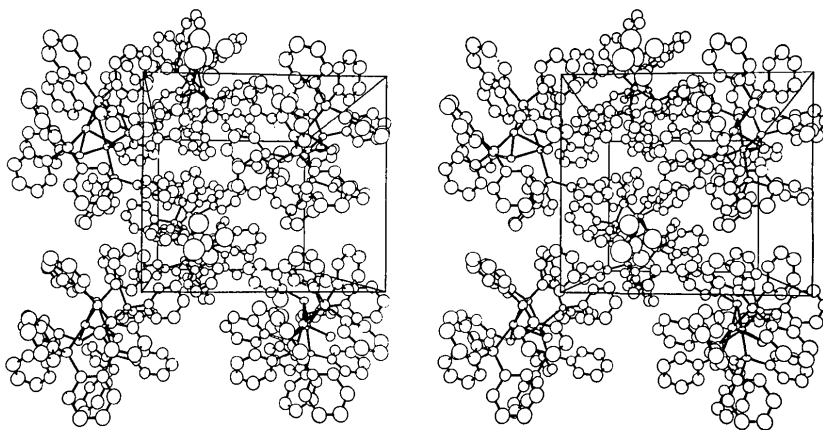
Fig. 4. Stereoscopic packing diagram. The view is down c, with a horizontal and b vertical.

bulky triphenylphosphine groups which form angles of 100·5 (2) and 99·5 (2)° at Ir(1) and Ir(2) respectively and between the Cl and S atoms of the bridge system which form average Cl–Ir–S angles of 76·5 (1)°. Because the phenyl rings were refined as rigid centro-symmetric planar groups, there are only 42 independent C–C lengths. These average 1·40 Å (r.m.s.d. 0·04 Å). The mean P–C and S–C lengths are 1·83 (3) and 1·74 (3) Å respectively, not significantly different from expected values (Kennard & Watson, 1973).

The thermal motion of the perchlorate anion and the three acetone molecules of solvation is very high. With U values ranging from 0·142 to 0·247 for the atoms of the solvent molecules, this part of the structure is clearly the least satisfying. In fact, certain genuine errors may exist. Classification of atoms as C or O was done on the basis of bond lengths calculated when the solvent molecules were first located on a difference map. Unfortunately these bond lengths have changed considerably during the refinement and the distinction between C and O atoms is no longer clear-cut.

Table 6. *Intermolecular contacts less than* 3·5 Å

O(2)···C(135')	3·474	O(4)·····C(334')	3·467
O(2)···C(24')	3·193	O(7)·····C(313')	3·296
O(3)···C(235')	3·412	C(135)···C(215')	3·351
O(4)···C(6')	3·217		

Consideration of the intermolecular contacts less than 3·5 Å, listed in Table 6, shows them to involve

primarily the O atoms of the perchlorate anion (see also Fig. 4). The acetone molecules are left with weaker, more remote interactions, resulting in high thermal motion and possibly even threefold disorder about the keto carbon atom.

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