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Crystal Structure of the Dimer of Rhodium Chloride 1,5-*cyclo*octadiene

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Rhodium(I) chloride 1,5-*cyclo*octadiene, $RhCl(C_8H_{12})$, crystallizes in the space group C_{2h}^5–$P2_1/n$, with four dimeric molecules in the unit cell of dimensions

$$a = 9{\cdot}05,\ b = 25{\cdot}4,\ c = 7{\cdot}28\ \text{Å};\ \beta = 91{\cdot}7°.$$

The crystal structure has been determined from three-dimensional Patterson and difference Fourier functions and has been refined by least-squares techniques. The conformation of the dimeric molecules suggested by Chatt & Venanzi is confirmed. Each rhodium atom is bonded to the double-bond centers of a *cyclo*octadiene ring (boat configuration) and to two chlorine atoms in such a way as to give it a square-planar configuration. The bonding in this compound is thus very different from that in $(RhCl(CO)_2)_2$, in which the rhodium atoms are described by Dahl, Martell & Wampler as octahedrally coordinated. The geometry of the *cyclo*octadiene rings is not too well defined in the present study. Nevertheless the lengthening of the double bonds from a 'normal' value of 1·34 Å to 1·44 ± 0·07 Å is significant, and is consistent with evidence based on the infrared spectra of the compound and of 1,5-*cyclo*octadiene.

Introduction

The present detailed investigation of the molecular and crystal structure of rhodium(I) chloride 1,5-*cyclo*octadiene was undertaken for two main reasons. First, Dahl, Martell & Wampler (1961) reported an unexpected structure for $(RhCl(CO)_2)_2$, in which each rhodium is described as octahedrally coordinated. The close parallelism between the physical properties of olefin complexes and carbonyl halides of transition metals has frequently been noted, and, in fact, Chatt & Venanzi (1957) remark on this parallelism in the case of $(RhCl(CO)_2)_2$ and rhodium chloride 1,5-*cyclo*octadiene. We thus thought it of interest to investigate the structure of rhodium chloride 1,5-*cyclo*octadiene, especially since we were unable to visualize a structure in which the rhodium atoms were octahedrally coordinated. A second reason for the present investigation was to attempt to answer the question: How well can carbon ring geometry be defined in the presence of second-row transition metals, if intensity data collected at room temperature and estimated visually are used? Previous studies (e.g., Baenziger, Doyle, Richards & Carpenter, 1961) have revealed that under these conditions the ring geometries are difficult to define accurately, but since such studies in general did not take account of anisotropy in the thermal vibrations of the heavy atoms it was not clear to us whether such poor definition results from inadequacies in the data or in the theoretical model.

In a preliminary communication (Ibers & Snyder, 1962) we indicated that the conformation of the rhodium chloride 1,5-*cyclo*octadiene dimeric molecule suggested by Chatt & Venanzi (1957) is correct: each rhodium atom is in a square-planar configuration. In the present paper we present the details of our study, define more thoroughly the structure, and indicate that the ring geometry is difficult to define even when anisotropic thermal motions of the heavy atoms are incorporated into the theoretical model.

Unit cell and probable space group

The crystals of rhodium chloride 1,5-*cyclo*octadiene used in the present study were kindly prepared by D. W. Barnum of these laboratories by the reaction of rhodium chloride trihydrate with the diene, as described by Chatt & Venanzi (1957). The deep yellow crystals exhibit a tabular habit. On the basis of calibrated precession photographs taken with Mo $K\alpha$ radiation $RhCl(C_8H_{12})$ crystallizes in a monoclinic cell of dimensions

$$a = 9{\cdot}05 \pm 0{\cdot}05,\ b = 25{\cdot}4 \pm 0{\cdot}1,\ c = 7{\cdot}28 \pm 0{\cdot}05\ \text{Å};$$
$$\beta = 91{\cdot}7 \pm 0{\cdot}2°.$$

The only systematic absences observed on over-exposed precession photographs of the $hk0$ and $h0l$ zones and on Weissenberg photographs of the $hk1$ through $hk6$ zones were: $0k0$, k odd; $h0l$, $h+l$ odd. Thus the space group is probably C_{2h}^5–$P2_1/n$, and a reasonable structure has been found on this assumption.

A density of $1{\cdot}93 \pm 0{\cdot}02$ g.cm.$^{-3}$ was measured pycnometrically. Water, with a small amount of Aerosol OT 75% wetting agent added, was used as

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the pycnometric fluid. The calculated density for eight monomer molecules of molecular weight 247 in the unit cell is 1·95 g.cm.$^{-3}$.

Hence the solution of the structure involves the location of two rhodium, two chlorine, and sixteen carbon atoms (and, of course, ideally the twenty-four hydrogen atoms).

Collection and reduction of intensity data

A crystal of approximate dimensions 0·06 × 0·02 × 0·003 cm. was chosen for the intensity work. The use of a crystal of this size is a reasonable compromise between possible absorption errors and convenient exposure times (Mo $K\alpha$ radiation). With a prismatic crystal the possibility exists that the absorption corrections to particular intensities may be large, even though the 'average' value of μR is small (about 0·3 here) and the angular range of the data limited ($\theta \leq 23°$ here). The reasonableness of the anisotropic thermal parameters of the heavy atoms (see below) is taken as an indication that absorption errors were not serious.

Since $RhCl(C_8H_{12})$ is stable, the selected crystal was simply attached to a quartz rod with silicone grease and mounted in air. Data for the *hk*0 through *hk*6 zones were collected at room temperature by the equi-inclination Weissenberg technique with the use of Mo $K\alpha$ radiation filtered through Zr foil. Exposures of the order of 1000 mA-hr. were taken. For each exposure the camera was loaded with three sheets of Ilford G Industrial X-ray film interleaved with copper sheets. The data were arbitrarily limited to the reflecting sphere $\lambda^{-1} \sin\theta \leq 0{\cdot}55$ Å^{-1}. The ratio of temperature-modified atomic scattering factors of Rh : Cl : C is about 30 : 6 : 1 on this sphere; we felt that data beyond this point would contribute only to the better resolution of the heavy atoms, possibly at the expense of the resolution of the light atoms.

The intensities were estimated visually by comparison with an intensity strip. This strip, which consisted of timed exposures of the (270) reflection, had a scale from 1 to 80, with 1 barely visible. Initially the intensities of only those reflections within the sphere $\lambda^{-1} \sin\theta \leq 0{\cdot}35$ Å^{-1} were estimated. Approximately 400 of the 600 independent reflections within this range were observed. From these data a successful trial structure was derived. Structure amplitudes based on this structure were of considerable aid in the indexing of those reflections between

$$0{\cdot}35 \leq \lambda^{-1} \sin\theta \leq 0{\cdot}55 \text{ Å}^{-1}.$$

Approximately 400 of the 1600 independent reflections within this range were observed and their intensities estimated. (The *hk*7 zone, which contains some reflections within this range, was not examined.)

Attempts to obtain useful correlation photographs with our precession camera were not successful, presumably because the severe requirements on crystal alignment and mechanical perfection of the instrument imposed by having the 25 Å *b* axis parallel to the Mo $K\alpha$ beam could not be met. Collection of Weissenberg data about the *b* axis was difficult because of the narrow screen slit required, and the collection of data about the *a* axis was unattractive because in this setting the short dimension of the crystal is along the rotation axis. For these reasons separate scale factors were carried for the seven zones *hk*0 through *hk*6. The use of separate scale factors hinders to some extent the determination of the anisotropic thermal parameters of the heavy atoms, but it may compensate partially for absorption errors.

Since least-squares refinements were contemplated, no attempt was made to obtain estimates of intensities for those inner reflections hidden by the Weissenberg beam stop.

The estimated intensities were multiplied by the appropriate Lorentz and polarization factors to yield relative values of the squares of the structure amplitudes. Neither extinction corrections nor absorption corrections were applied to these data. The structure amplitudes were not scaled initially; the final scaling (Table 2) is based on the calculated structure amplitudes.

Solution of the structure

A successful trial structure was found very readily by standard methods. The rhodium and chlorine positions were located on a three-dimensional Patterson* map which was based on the 400 inner reflections. The resultant four-membered ring of two rhodiums and two chlorine atoms confirmed the dimeric nature of the compound, originally inferred from molecular weight and magnetic susceptibility measurements by Chatt & Venanzi (1957). These heavy-atom positions, together with guessed-at isotropic thermal parameters and a single scale factor, were refined in one cycle of least squares. The resultant values of $F_o - F_c$ were used in the calculation of a three-dimensional difference Fourier. On this Fourier map seventeen peaks whose heights were greater than one-half the maximum electron density were found, and sixteen of these were assigned to carbon atoms on the basis of a cork-ball model of the molecular structure. Convergence of a least-squares refinement, based on the heavy-atom parameters previously obtained together with the assigned carbon-atom positions, a single scale factor, and an assumed isotropic thermal parameter for all carbon atoms, was an indication that the correct structure had been found. The struc-

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* We are grateful to Dr A. Zalkin, Lawrence Radiation Laboratory, University of California, for making available his Fourier series program for the IBM 704. This program, when used with the 'Compatibility Package' on the IBM 7090, requires about 20 min. of machine time for 800 reflections and 50,000 grid points.

ture is that proposed by Chatt & Venanzi (1957), and described below (Fig. 1).

Refinement of the structure

Refinement of the structure was carried out almost entirely by least-squares techniques. Since no reflections were observed independently more than once the weighting scheme suggested previously (Ibers, 1956) could not be employed; rather, a scheme designed to be a smoothed approximation to weight(F) inversely proportional to the variance(F) was adopted. The scheme allotted constant weight for $F \leq 3\cdot5F_{\min}$, and weight proportional to F^{-2} for $F > 3\cdot5F_{\min}$. This is essentially the scheme devised by Hughes (1941). Although different, 'reasonable' weighting schemes may result in different bond distances, such differences will probably not be significant (cf. e.g. Ibers & Cromer, 1958; Baenziger, Doyle, Richards & Carpenter, 1961). Refinements were based on F, not F^2 and on observed reflections only. The Busing–Levy (1959*a*) least-squares program for the IBM 704, with special patches as necessary, was used with the 'Compatibility Package' on the IBM 7090. In this way about a threefold advantage in speed is realized over calculations on the 704. In the present case one cycle of full-matrix least-squares (800 data, 87 parameters, isotropic thermal parameters) requires about 8 min. of machine time.

For the calculation of structure factors the atomic scattering factors for Rh, Cl, and C of Thomas & Umeda (1957), Dawson (1960), and Hoerni & Ibers (1954) were used. A correction for anomalous dispersion was applied to the rhodium atom scattering factor (Templeton, 1962).

The initial refinement was based on all of the observed reflections, on separate scale factors for the individual zones, and on individual isotropic thermal parameters for all atoms. Thus there were 87 parameters to be determined from the 779 non-zero reflections. (The presence of hydrogen atoms in the structure was ignored in this and in subsequent refinements.) This refinement converged after several cycles to a structure in which the C–C single bonds ranged from 1·2 to 1·8 Å in length. A difference Fourier, in which the F_c of the heavy atoms were subtracted from F_o, was then calculated. The carbon atom positions on this difference Fourier were far better resolved than they were on the initial difference Fourier. The general agreement between these positions and those of the least-squares was not too good; some positions deviated by as much as 0·3 Å from the least-squares positions.* Contrary to the experience of others

Table 1. *Atomic parameters for* $(\mathrm{RhCl(C_8H_{12})})_2$*

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Rh	0·3894	0·0004	0·3248	0·0002	0·4347	0·0005	2·21	0·10
Rh′	0·6419	0·0004	0·4137	0·0001	0·6342	0·0005	2·39	0·10
Cl	0·4242	0·0015	0·3677	0·0006	0·7225	0·0018	3·71	0·30
Cl′	0·6241	0·0014	0·3605	0·0006	0·3645	0·0020	3·81	0·30
1	0·394	0·006	0·265	0·002	0·236	0·008	4·8	1·4
2	0·318	0·004	0·314	0·002	0·164	0·006	2·0	0·9
3	0·154	0·008	0·327	0·003	0·119	0·010	7·3	1·8
4	0·080	0·007	0·317	0·003	0·286	0·010	6·5	1·7
5	0·155	0·006	0·317	0·002	0·487	0·008	4·4	1·2
6	0·238	0·005	0·272	0·002	0·544	0·007	3·1	1·0
7	0·236	0·005	0·215	0·002	0·440	0·007	3·4	1·1
8	0·299	0·005	0·219	0·002	0·270	0·007	3·3	1·1
1′	0·870	0·005	0·431	0·002	0·597	0·008	3·6	1·2
2′	0·787	0·006	0·468	0·002	0·510	0·009	4·7	1·3
3′	0·773	0·007	0·526	0·002	0·600	0·009	5·5	1·5
4′	0·649	0·010	0·529	0·004	0·753	0·015	10·8	2·8
5′	0·595	0·005	0·474	0·002	0·831	0·007	2·8	1·0
6′	0·695	0·005	0·436	0·002	0·912	0·007	3·4	1·2
7′	0·858	0·006	0·439	0·002	0·954	0·009	4·9	1·4
8′	0·925	0·006	0·438	0·002	0·790	0·009	5·2	1·5

Atom	β_{11}	$\sigma(\beta_{11})$	β_{22}	$\sigma(\beta_{22})$	β_{33}	$\sigma(\beta_{33})$	β_{12}	$\sigma(\beta_{12})$	β_{13}	$\sigma(\beta_{13})$	β_{23}	$\sigma(\beta_{23})$
Rh	0·0056	0·0004	0·0010	0·0001	0·0105	0·0008	−0·0001	0·0002	−0·0003	0·0005	−0·0001	0·0002
Rh′	0·0077	0·0005	0·0009	0·0001	0·0113	0·0009	−0·0004	0·0002	−0·0003	0·0005	−0·0001	0·0002
Cl	0·0146	0·0021	0·0016	0·0003	0·0121	0·0032	−0·0024	0·0006	0·0018	0·0019	−0·0012	0·0007
Cl′	0·0124	0·0020	0·0014	0·0003	0·0201	0·0038	−0·0010	0·0006	0·0031	0·0020	−0·0010	0·0008

* The positional parameters of all the atoms and the anisotropic thermal parameters of the heavy atoms are based on the anisotropic refinement in which the isotropic thermal parameters of the carbon atoms given here were held constant. The isotropic thermal parameters of the heavy atoms given here are those derived from the isotropic refinement.

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* The peak centers were calculated with the use of an IBM 7090 program based on the 27 point least-squares method of Shoemaker *et al.* (1950). Since the grid spacing was about 0·2 Å and since the peaks overlap slightly, the uncertainty in the positions of the peak centers is probably about 0·1 Å

(e.g. Rossmann *et al.*, 1959) the thermal parameters of the misplaced carbon atoms were not significantly larger than the average. A final refinement with isotropic thermal parameters and the carbon atoms relocated in accordance with the positions of the difference Fourier converged rapidly to a structure with more reasonable bond distances. The value of the R factor, $(\Sigma|F_o-|F_c||/\Sigma F_o)$, was 0·101 for the 779 non-zero reflections; the error of fit function $(\Sigma w(F_o-|F_c|)^2/(m-n))^{\frac{1}{2}}$ had the value 7·15.

The difference Fourier provided evidence that the heavy atoms, particularly the chlorine atoms, were vibrating anisotropically. On the assumption that proper account of such motion would lead to improved positions for the carbon atoms, a refinement based on anisotropic thermal parameters of the heavy atoms was attempted. The first attempt, in which the positional parameters of all the atoms, the six independent thermal parameters of each of the heavy atoms, and the scale factors were varied, was unsuccessful: physically unreasonable shifts in the scale factors were obtained. We had failed to realize that since the scale factors and the β_{33} of the heavy atoms depend only upon l, and since the heavy atoms are the principal contributors to the structure amplitudes, the least squares matrix of normal equations is nearly

Table 2. *Observed and calculated structure factors*

H	K	OBS	CAL
*****L=0*****			
0	00	A	871.2
2	00	064	-078
4	00	299	-299
8	00	104	094
2	01	046	056
3	01	100	-136
4	01	066	087
5	01	075	-095
7	01	064	062
8	01	070	-068
0	02	B	-036
1	02	059	-047
2	02	026	-016
3	02	041	056
5	02	075	090
6	02	049	052
7	02	045	-045
9	02	053	-057
1	03	B	-176
2	03	138	-146
3	03	088	083
4	03	051	067
5	03	107	116
6	03	079	084
9	03	066	-059
0	04	B	-147
1	04	B	-290
2	04	090	-070
3	04	272	-210
4	04	154	151
5	04	134	121
7	04	064	067
1	05	028	-035
2	05	079	-077
3	05	086	074
5	05	046	-047
6	05	041	039
0	06	C	037
1	06	036	033
2	06	048	061
3	06	031	029
4	06	033	-022
5	06	054	-058
6	06	095	-084
1	07	046	051
2	07	202	173
3	07	041	047
5	07	039	-041
6	07	115	-102
0	08	190	-174
1	08	196	160
3	08	094	086
4	08	129	109
5	08	090	-086
2	09	050	057
4	09	039	-038
5	09	042	038
0	10	C	015
3	10	036	-040
7	10	048	057
1	11	081	079
3	11	117	-121
4	11	039	-044
5	11	042	-042
7	11	060	062
0	12	156	145
1	12	098	086
3	12	039	051
4	12	157	-145
8	12	066	065
1	13	036	037
3	13	048	-053
0	14	C	-029
1	14	046	-048
5	14	057	053
1	15	039	-042
2	15	154	-167
3	15	041	039
5	15	C	049
6	15	098	097
0	16	C	-013
1	16	130	-134
2	16	041	045
3	16	106	-101
5	16	089	087
7	16	066	069
3	17	054	040
7	17	054	-049
0	18	080	-066
1	18	086	087
3	18	055	062
1	19	090	-089
2	19	136	136
3	19	058	058
5	19	062	061
6	19	091	-089
0	20	138	-118
4	20	071	067
5	20	073	-066
0	22	129	113
4	22	064	-075
1	23	086	089
3	23	063	-069
5	23	054	-064
0	26	C	-059
2	27	080	-065
*****L=+1*****			
1	00	B	-032
3	00	155	-181
5	00	038	-047
7	00	103	098
0	01	B	196
1	01	B	073
2	01	071	-083
4	01	044	-056
6	01	055	053
7	01	069	-071
0	02	B	-070
1	02	B	-071
4	02	076	076
5	02	056	067
8	02	074	-055
9	02	070	-056
0	03	B	-177
1	03	B	-212
2	03	093	-085
3	03	055	050
4	03	102	123
5	03	070	081
8	03	065	-059
0	04	194	-233
1	04	164	-145
2	04	195	-169
3	04	045	059
4	04	103	116
6	04	078	087
1	05	036	-040
4	05	054	-057
5	05	058	062
6	05	065	-066
8	05	066	053
0	06	030	034
1	06	103	101
2	06	091	090
5	06	125	-124
6	06	045	-043
9	06	109	092
1	07	220	196
2	07	131	113
3	07	055	062
5	07	120	-109
6	07	087	-069
0	08	186	165
1	08	054	059
2	08	062	073
3	08	165	143
4	08	088	-095
5	08	044	038
8	08	055	045
0	09	082	-073
1	09	038	040
3	09	091	-097
4	09	070	075
7	09	103	096
1	10	048	-057
2	10	076	-077
3	10	060	-060
4	10	066	-067
5	10	055	040
6	10	091	.088
8	10	069	073
0	11	146	143
2	11	143	-147
3	11	038	-026
4	11	120	-112
6	11	059	060
2	12	048	053
3	12	187	-189
4	12	054	046
6	12	049	-058
7	12	076	070
8	12	056	-043
2	13	049	-047
3	13	126	119
6	13	051	049
7	13	095	-100
3	14	062	063
4	14	073	064
0	15	092	-076
1	15	147	-141
2	15	113	109
3	15	044	-038
4	15	058	062
5	15	093	096
0	16	095	-090
2	16	132	-128
4	16	048	046
6	16	077	079
1	17	045	-047
6	17	067	-071
2	18	048	063
5	18	054	-049
0	19	088	-091
1	19	143	132
0	23	085	091
1	27	059	-071
*****L=-1*****			
1	00	B	407
3	00	076	-058
5	00	181	-242
7	00	058	056
9	00	056	071
1	01	B	063
2	01	051	044
3	01	051	064
4	01	147	-163
5	01	048	049
6	01	054	-048
7	01	058	-057
8	01	074	077
9	01	056	-049
4	02	044	048
8	02	065	-072
3	03	142	-131
4	03	164	163
6	03	054	059
7	03	059	058
1	04	074	-080
2	04	170	-154
3	04	146	124
4	04	184	-172
5	04	081	092
6	04	100	.116
8	04	054	056
1	05	030	-025
3	05	150	-153
4	05	069	070
6	05	045	-045
7	05	092	083
1	07	041	049
2	07	110	-109
3	07	258	203
7	07	087	-100
1	08	232	-195
2	08	231	187
3	08	071	-062
4	08	084	084
5	08	096	098
6	08	099	-097
1	09	030	-019
2	09	044	-045
3	09	069	068
4	09	056	059
6	09	048	047
1	10	082	078
2	11	169	163
4	11	136	-123
6	11	069	-059
1	12	188	196
2	12	055	052
5	12	122	-117
2	13	038	028
4	13	044	-040
1	14	070	-067
2	14	051	-053
1	15	041	-031
2	15	067	-074
3	15	172	-145
6	15	054	046
7	15	069	071
1	16	054	-043
2	16	093	-105
4	16	067	-065
6	16	066	070
2	18	081	080
3	19	093	093
4	19	063	073
1	20	078	-078
2	20	049	056
5	20	067	069
1	22	063	078
5	22	071	-072
4	23	091	-091
1	24	055	056
*****L=+2*****			
2	00	B	-196
6	00	097	092
0	01	B	041
1	01	B	-104
2	01	077	066
5	01	051	062
6	01	121	-119
0	02	B	-045
1	02	B	038
3	02	045	057
4	02	052	070
5	02	072	-088
7	02	080	-074
8	02	066	-070
9	02	058	060
0	03	B	-117
1	03	B	-044
2	03	028	021
3	03	136	121
4	03	052	055
5	03	042	031
6	03	046	-042
7	03	062	-054
9	03	059	-048
1	04	197	-213
2	04	056	058
3	04	087	086
5	04	136	124
6	04	046	-044
0	05	121	-116
1	05	131	126
2	05	046	-053
3	05	034	-047
4	05	100	109
5	05	104	-122
9	05	073	066
0	06	101	080
1	06	034	036
2	06	058	066
3	06	045	042
4	06	138	-133
8	06	111	098
0	07	243	188
1	07	046	050
2	07	091	093
3	07	056	066
4	07	074	-069
5	07	062	-086
6	07	067	-057
9	07	059	045
0	08	126	-116
1	08	143	132
2	08	131	114
3	08	079	-086
4	08	091	104
5	08	080	-082
6	08	049	-048
0	09	133	120
1	09	039	-038
2	09	114	-103
3	09	077	071
4	09	125	-120
5	09	079	075
6	09	098	085
1	10	059	-061
2	10	069	-068
3	10	118	-123
5	10	046	046
7	10	093	085
1	11	088	-079
2	11	046	-054
3	11	132	-131
6	11	051	038
0	12	070	067
1	12	037	035
2	12	166	-143
3	12	084	084
4	12	045	-042
6	12	051	059
2	13	133	126
4	13	046	045
5	13	049	064
6	13	074	-084
0	14	070	-074
2	14	042	042
3	14	077	086
4	14	067	070
0	15	104	-104
3	15	056	062
4	15	059	074
1	16	083	-098
1	17	056	074
0	18	058	056
1	18	058	061
4	18	065	-067
0	19	077	086
1	19	049	052
2	21	052	-050
2	22	066	-057
3	23	070	-064
0	27	074	-081
*****L=-2*****			
2	00	B	080
4	00	034	-036
6	00	110	-113
8	00	066	067
1	01	B	056
3	01	066	065
4	01	051	054
5	01	070	-090
9	01	070	057
4	03	140	-140
5	03	051	061
1	04	069	066
2	04	088	-063
3	04	205	-158
4	04	058	053
5	04	051	-053
7	04	093	109
2	05	028	-030
4	05	114	-122
8	05	077	084
2	06	052	-048
3	06	049	052
1	07	122	-097
2	07	090	084
3	07	093	-103
4	07	164	164
5	07	080	078
8	07	067	-095
1	08	142	-130
2	08	168	-156
3	08	206	166
4	08	049	042
5	08	052	058
6	08	101	109
7	08	104	-106
1	09	105	-102
3	09	037	-035
4	09	042	045
5	09	063	060
1	10	069	-062
2	10	108	113
3	10	049	-055
6	10	059	-062
1	11	230	233
3	11	121	112
5	11	150	-154
7	11	066	-071
2	12	201	198
4	12	055	-058
6	12	125	-118
2	13	039	043
1	14	051	068
2	14	090	-079
1	15	095	-108
4	15	102	-104
5	15	072	072
2	16	055	-054
3	16	088	-092
3	18	060	053
4	19	076	079
2	20	051	-045
3	20	052	060
2	22	066	056
1	23	079	076
2	24	070	070
*****L=+3*****			
1	00	B	-209
5	00	052	061
0	01	B	-074
1	01	B	182
2	01	112	-087
4	01	046	044
5	01	151	-151
9	01	075	068
0	02	B	070
1	02	B	-051
2	02	221	173
3	02	082	079
4	02	072	-072
6	02	125	-129
1	03	B	030
2	03	160	137
3	03	075	084
4	03	047	053
5	03	069	-076
6	03	059	-053
0	04	B	-197
1	04	141	135
2	04	035	024
4	04	116	109
5	04	043	-052
0	05	155	172
1	05	168	-139
2	05	032	-031
3	05	056	053
4	05	139	-134
5	05	063	068
8	05	069	076
1	06	072	061
3	06	139	-124
5	06	053	-070
7	06	075	092
0	07	035	032
1	07	082	073
3	07	060	-059
4	07	078	-090
5	07	046	-062
0	08	175	158
1	08	056	063
2	08	050	-038
3	08	072	059
4	08	043	-065
0	09	052	-056
1	09	065	-062
2	09	046	054
3	09	088	-069
4	09	075	075
5	09	057	063
6	09	050	-038
0	10	C	-016
1	10	057	-065
2	10	108	-099
6	10	082	083
1	11	059	-063
2	11	111	-096
5	11	047	042
6	11	052	056
0	12	053	037
1	12	088	-090
5	12	050	059
0	13	057	-070
1	13	057	060
4	13	082	076
5	13	050	-068
2	14	063	068
3	14	080	074
2	15	046	040
3	15	075	075
0	16	065	-071
3	16	059	-064
0	17	095	092
2	17	047	-043
4	17	085	-094
0	18	062	061
1	18	050	057
3	18	063	-064
3	19	053	-053
2	20	075	-068
3	20	068	060
1	21	066	-074
5	21	060	075
1	22	056	-054
2	23	070	-074
2	24	059	051
*****L=-3*****			
1	00	B	084
3	00	184	190
5	00	059	-061
7	00	108	-103
1	01	B	021
2	01	108	102
3	01	046	048
4	01	065	081
6	01	057	-067
2	02	065	069
1	03	B	077
2	03	105	-104
4	03	037	-037
5	03	078	-087
3	04	095	-117
4	04	151	-178
7	04	052	046
8	04	088	089
1	05	132	111
3	05	053	-076
4	05	062	-070
5	05	075	-072
1	06	099	089
1	07	106	-112
2	07	046	-050
3	07	068	075
5	07	095	091
1	08	135	-122
2	08	043	-046
3	08	053	-053
4	08	092	112
5	08	111	087
6	08	050	033
7	08	075	064
8	08	082	-078
1	09	131	-116
2	09	057	-060
6	09	060	045
2	10	059	-069
3	10	049	048
2	11	138	144
3	11	050	-045
6	11	137	-123
1	12	060	069
3	12	121	105
5	12	092	-080
7	12	089	-079
1	13	040	036
1	14	079	-089
2	14	069	067
5	14	063	057
1	15	099	098
2	15	056	-057
5	15	082	-079
6	15	068	074
4	16	108	-095
1	19	072	-071
2	19	052	-043
5	19	082	078
3	22	057	071
2	23	091	085
*****L=+4*****			
0	00	B	-093
2	00	068	-073
4	00	045	033
0	01	B	118
1	01	B	-090
2	01	084	091
3	01	030	031
4	01	102	-088
6	01	045	-053
1	02	B	190
2	02	086	086
4	02	035	041
5	02	133	-123
6	02	056	-045
1	03	B	078
2	03	114	104
3	03	065	060
0	04	B	077
3	04	057	058
4	04	038	-034
0	05	C	-075
3	05	102	-117
7	05	087	083
0	06	C	073
2	06	142	-135
3	06	044	-043
4	06	083	-078
6	06	094	096
0	07	C	077
2	07	068	-069
3	07	067	-067
4	07	049	-045
0	08	048	046
1	08	038	-038
2	08	041	040
0	09	072	-063
1	09	061	060
3	09	061	056
4	09	093	085
1	10	112	-110
3	10	068	065
5	10	102	108
1	11	080	-089
4	11	044	043
0	12	098	-094
4	12	054	046
0	13	072	075
3	13	053	054
4	13	091	-099
1	14	057	057
2	14	079	081
5	14	061	-063
6	14	053	-053
2	15	069	069
3	16	057	066
4	16	049	-045
3	17	108	-111
0	18	057	061
2	18	048	-049
2	19	049	-042
1	20	061	-064
2	20	063	058
0	21	063	-054
2	21	064	-064
*****L=-4*****			
2	00	110	135
4	00	135	154
6	00	125	-105
8	00	112	-092
1	01	B	-029
2	01	064	068
3	01	125	137
4	01	071	073
7	01	084	-083
2	02	056	-061
3	02	118	129
1	03	042	-057
2	03	131	130
3	03	142	-123
6	03	045	-061
7	03	068	069
1	04	128	128
2	04	080	-065
4	04	090	-077
5	04	143	-122
8	04	053	049
1	05	113	098
2	05	041	048
4	05	083	-077
5	05	057	-057
6	05	045	-044
1	06	060	-054
2	06	116	111
1	07	093	094
2	07	069	-066
4	07	072	060
6	07	056	060
1	08	080	-081
2	08	041	-044
5	08	091	086
2	09	033	-035
3	11	068	070
7	11	065	-069
1	12	038	-042
2	12	038	043
4	12	054	067
1	13	054	-063
2	14	050	-063
2	15	080	088
4	15	067	-063
6	15	053	-056
1	16	093	091
5	16	080	-080
1	17	084	085
1	18	048	-051
*****L=+5*****			
1	00	B	-053
3	00	031	028
0	01	B	-050
1	01	B	068
3	01	058	-053
5	01	052	-054
0	02	B	078
1	02	B	069
3	02	063	051
4	02	078	-086
5	02	052	-049
1	03	B	063
2	03	058	064
6	03	059	-057
2	04	031	032
2	05	121	-117
6	05	085	090
1	06	103	-108
3	06	082	-073
5	06	085	087
2	07	059	-061
6	07	051	053
1	08	047	056
1	09	085	-091
2	09	079	076
3	09	080	077
5	09	075	072
6	09	051	-059
0	10	124	-129
4	10	118	107
5	10	049	-043
0	11	069	-060
0	12	079	083
4	12	058	-059
1	13	078	072
3	13	079	-088
5	13	080	-074
0	14	080	085
1	14	051	056
4	14	086	-088
2	17	092	-094
*****L=-5*****			
3	00	093	089
5	00	066	047
7	00	101	-089
1	01	B	-046
3	01	055	058
4	01	063	067
3	02	063	-061
4	02	073	075
2	03	076	-077
3	03	104	097
4	03	047	-049
6	03	047	058
2	04	092	096
6	04	066	-076
2	05	089	089
3	05	034	037
1	06	080	073
2	06	076	-078
3	06	086	080
5	06	062	-049
1	07	080	-080
2	07	087	076
5	07	070	071
6	07	049	-044
2	08	034	-039
3	08	047	-054
6	08	069	072
1	09	063	064
2	09	051	-047
3	09	047	-048
1	10	051	-058
4	10	062	-058
5	10	047	048
4	11	094	085
1	12	056	-069
3	12	062	059
5	12	049	062
1	13	092	-099
3	14	056	-060
3	15	047	051
2	16	066	075
2	17	078	069
*****L=+6*****			
0	00	B	-041
0	01	B	056
2	01	068	-077
4	01	074	-068
0	02	B	044
2	02	054	052
3	02	110	-106
1	03	B	073
2	03	042	-036
5	03	077	-071
1	05	078	-097
5	05	085	082
0	06	049	-054
2	06	093	-099
4	06	071	058
6	06	070	073
1	07	063	-075
5	07	057	054
0	09	096	-111
1	09	065	074
4	09	070	060
3	10	084	078
0	12	C	-015
0	13	086	082
4	13	059	-066
1	17	077	-078
*****L=-6*****			
2	01	061	-062
1	02	B	-070
2	02	033	-038
3	03	046	-050
3	04	067	065
3	05	102	092
2	06	082	075
2	07	042	-047
3	08	054	-053
4	08	050	-055
3	09	063	-050
4	09	067	-079
1	10	088	085
2	10	046	-043
5	10	067	-066
5	11	077	070
1	12	056	-060
4	12	056	051
2	13	052	-049
4	13	067	059
1	14	074	-073
4	14	049	-047

A-F(CAL) ARE IN ELECTRONS. HYDROGEN ATOM CONTRIBUTIONS ARE NOT INCLUDED.
B-REFLECTION HIDDEN BY THE BEAM STOP.
C-REFLECTION OBSCURED BY RADIATION STREAK OR BY FILM IMPERFECTION.

Table 3. *Root-mean-square thermal displacements (in Å)**

	Root-mean-square displacement				
Atom	Max.	Int.	Min.	⊥ to Rh, Cl plane	In Rh, Cl plane
Rh	0·18	0·17	0·15	isotropic	
Rh′	0·19	0·18	0·16	isotropic	
Cl	0·29	0·18	0·16	0·28	0·17, isotropic
Cl′	0·27	0·20	0·19	0·27	0·20, isotropic

* Estimated standard deviations: Rh, 0·01 Å; Cl, 0·02 Å.

singular.† In the succeeding refinement the scale factors from the isotropic refinement were used and were not varied. The thermal parameters of the carbon atoms from the isotropic refinement were held constant in this refinement, for attempts to vary these while varying the thermal parameters of the heavy atoms anisotropically led to physically unreasonable thermal parameters for the carbon atoms. The anisotropic refinement (84 parameters) converged to a reliability factor of 0·096 and to a value of 6·88 for the error of fit function. The final parameters from this refinement (with carbon atom thermal parameters from the isotropic refinement) are listed in Table 1. The values of F_c based on these data, together with the values of F_o for observed and obscured reflections, are listed in Table 2. The F_c values accordingly do not include the contributions from hydrogen atoms. The F_o values have been scaled absolutely with the use of the scale factors from the isotropic refinement. A check of the structure amplitudes of the approximately 1400 unobserved reflections within the sphere $\lambda^{-1}\sin\theta < 0{\cdot}55$ Å^{-1} revealed none which we deem to exceed significantly (10% level) our estimates of $F_{\min}$. Therefore these data are not listed in Table 2.

None of the positional parameters from the anisotropic refinement differs significantly (15% level) from the parameters obtained from the isotropic refinement. Similarly, the improvement in the reliability factor is not significant (Hamilton, 1961). The reason for this lack of improvement, which is contrary to general experience, is apparent from the ellipsoids of vibration of the heavy atoms (Table 3). In agreement with expectations, the chlorine atoms are vibrating with considerably greater amplitudes normal to the rhodium–chlorine planar ring than in it. However, the vibrations of the rhodium atoms are essentially isotropic. This we believe is reasonable on the basis of the molecular structure. Since the rhodium atoms are vibrating isotropically, little improvement in agreement between observed and calculated structure amplitudes should result when the heavy atoms are allowed to vibrate anisotropically. Incidentally, the values of the reliability factor and error of fit function for F_c calculated with omission of the carbon-atom contributions and with (*a*) isotropic thermal parameters and (*b*) anisotropic thermal parameters on the heavy atoms are (*a*) 0·162 and 12·09, and (*b*) 0·157 and 11·88.

Since the anisotropic thermal parameters are sensitive to systematic errors in the data, the results of Table 3 would seem to indicate, insofar as they agree with our expectations concerning the nature of the vibrations of atoms in the molecule, that systematic errors in the data are not serious. On the other hand, systematic errors in the data might possibly be the explanation for the thermal parameter of atom 4′ (Table 1). (See Fig. 1 for the designation of atoms.) The isotropic thermal parameter of atom 4′ is significantly higher (at the 1% level) than the mean value of $4{\cdot}3 \pm 1{\cdot}4$ Å^2 derived from the individual thermal parameters of the other fifteen carbon atoms. (None of these differs significantly from another.) There is no structural explanation for this. Of course, the high thermal parameter might indicate that atom 4′ is misplaced slightly from minimum position (Rossmann *et al.*, 1959). Because of this, and because the data of Table 1 lead to rings with obvious distortions, further refinements were attempted in which particular carbon atoms, such as 4′, or particular groups of carbon atoms, were deliberately displaced from the positions of Table 1 to 'more reasonable' positions. In all cases after a few cycles the atomic positions were those of Table 1. This result, while it provides no explanation for the high thermal parameter value for 4′, is comforting, for it makes it seem likely that the refinement has converged to a true minimum in multi-dimensional space. A check of the correlation matrix reveals no unusual correlations between B of atom 4′ and other variables. As mentioned above systematic errors in the data might be the explanation for the high thermal parameter of atom 4′. However, on the Fourier map, which is based on a weighting scheme very different from that used in the least-squares calculation, the peak height of atom 4′ is only about 75% of the average peak height of the carbon atoms. Thus, we offer no positive reason for the high value of the thermal parameter of atom 4′.

As indicated in the next section, the data of Table 1 lead to rings which are distorted, although the distortions are not significant when account is taken of the uncertainties in the positions of individual carbon atoms. Although it would be of great interest to compare the present results with those based on a model in which the rings were constrained to have certain

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† We are indebted to Prof. D. H. Templeton for a discussion in which he pointed this fact out to us.

dimensions, the present case was not deemed to be a favorable one for a refinement with constraints. Such a refinement would be sensible (although it would involve much labor) for a problem in which the data were more reliable than here and in which the contributions of the atoms in the rings to the structure amplitudes were greater than they are here.

Description of the structure

The structure defined by the parameters of Table 1 and by the equivalent positions of the space group is one in which individual molecules of $(RhCl(C_8H_{12}))_2$ of conformation depicted in Fig. 1 pack together tightly, with a given *cyclo*octadiene ring in contact with rings from three or four adjacent molecules. The *cyclo*octadiene rings have the boat configuration. Each rhodium atom is in an approximately square-planar configuration, being bonded to two chlorine atoms and to the double-bond centers of a *cyclo*octadiene ring (Fig. 2). The closest approaches of carbon atoms from other molecules to a given rhodium atom are 3·79, 4·03, and 4·07 Å in directions not normal to the plane of the double-bond centers, chlorine atoms, and rhodium atoms. Thus there is no evidence for a configuration other than dsp^2 for the rhodium atoms. This configuration is markedly different from that found by Dahl *et al.* (1961) for the rhodium atoms in $(RhCl(CO)_2)_2$. The properties and reactions of these two compounds are similar, and thus one is reminded that it is often difficult to correlate molecular structure with physical properties.

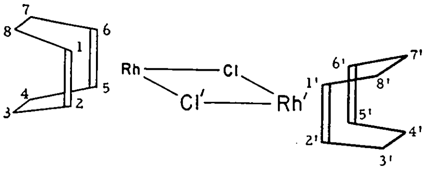

Fig. 1. Sketch of the (RhCl-1,5-*cyclo*octadiene)$_2$ molecule. The rhodiums, chlorines, and double-bond centers are nearly coplanar.

There are two imperfections in the square-planar arrangement of the rhodium atoms. First, a given rhodium atom is closer to the double-bond centers (2·00 Å) than to the chlorine atoms (2·38 Å), but the bond angles are only slightly different from 90° (Fig. 2). Second, the double-bond centers, chlorine atoms, and rhodium atoms do not lie exactly in a plane. In Table 4 the equation of the formal (unit weight) least-squares plane is given, together with the deviations of the individual atoms and double-bond centers from this plane. Only the deviations of the chlorine atoms are significant (at the 1% level); the two rhodium atoms and four double-bond centers do not deviate significantly from the plane. The double bonds are normal to this plane, within the accuracy with which their directions are determined in this study.

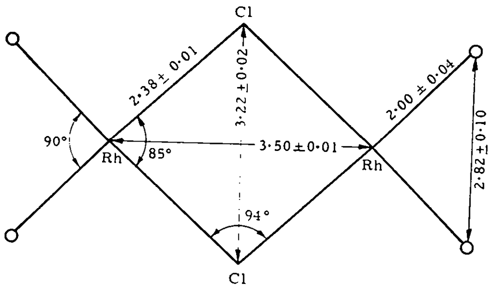

Fig. 2. Principal bond distances (Å) and angles between the Rh, Cl, and double-bond centers (symbolized by ○).

The packing of the molecules is tight. There is one C–C intermolecular contact (between symmetry related 5′ atoms) which is 3·3 Å; all other C–C intermolecular contacts are 3·7 Å or longer. There are some Cl–C intermolecular contacts as short as 3·65 Å. Such close packing may be the explanation for the deviations of the chlorine atoms from the least-squares plane.

Table 4. *Deviations (in Å) of atoms and double-bond centers from least-squares plane*

Atom or center	Deviation	Atom or center	Deviation
Rh	−0·010	1–2	0·12
Rh′	−0·003	5–6	0·04
Cl	−0·16	1′–2′	0·08
Cl′	−0·19	5′–6′	0·11

Equation of unit normal to the formal (unit weight) least-squares plane is

$$\mathbf{m} = -4{\cdot}589\mathbf{b}_1 + 19{\cdot}381\mathbf{b}_2 - 2{\cdot}805\mathbf{b}_3$$

where the $\mathbf{b}_i$'s are the reciprocal lattice vectors. The origin to plane distance is 3·355 Å. Least-squares plane was based on equation (11) of Schomaker *et al.* (1959).

Table 5 lists selected intramolecular bond distances and angles. These have been computed with the help of the Busing–Levy (1959*b*) error function program from the final least-squares output tape. The standard deviations attached to individual distances and angles are those derived in this way from the complete inverse error matrix and so include the effects of correlation between variables. In Table 5 there are also given for a given set of distances or angles, mean bond distances or mean bond angles, together with the standard deviation of an individual member of the set on the assumption of equivalence. There are no significant deviations (5% level) of members of a given set from the mean of the set, and so the ensuing discussion is limited to mean distances and angles. Similarly, the distances and angles depicted in Fig. 2 are mean values.

The Rh–Cl distance of 2·38 ± 0·01 Å is within the range of 2·32 to 2·41 Å tabulated by Baenziger *et al.* (1961) for Pt–Cl and Pd–Cl distances. The distance also compares well with the Rh–Cl distances of 2·33

Table 5. *Selected intramolecular bond distances (in Å) and angles*

Distance A–B

A–B	$d(A$–$B)$	$\sigma(d(A$–$B))$	A–B	$d(A$–$B)$	$\sigma(d(A$–$B))$
Rh–Rh′	3·498	0·005	Cl–Cl′	3·22	0·02
Rh–Cl	2·37	0·01	Rh–3	3·09	0·06
Rh–Cl′	2·38	0·01	Rh–4	2·98	0·06
Rh′–Cl	2·39	0·01	Rh–7	3·12	0·05
Rh′–Cl′	2·39	0·01	Rh–8	3·04	0·05
	2·38	0·01	Rh′–3′	3·10	0·06
			Rh′–4′	3·05	0·10
			Rh′–7′	3·07	0·06
Rh–1	2·10	0·06	Rh′–8′	2·84	0·06
Rh–2	2·07	0·04		3·04	0·09
Rh–5	2·18	0·05			
Rh–6	2·10	0·05			
Rh′–1′	2·13	0·05	1–2	1·52	0·07
Rh′–2′	2·13	0·06	5–6	1·42	0·07
Rh′–5′	2·14	0·05	1′–2′	1·36	0·07
Rh′–6′	2·14	0·05	5′–6′	1·44	0·06
	2·12	0·03		1·44	0·07
2–3	1·54	0·04	1–6	2·69	0·08
3–4	1·43	0·09	2–5	2·81	0·07
4–5	1·59	0·09	1′–6′	2·82	0·07
6–7	1·63	0·07	2′–5′	2·95	0·08
7–8	1·39	0·07		2·82	0·10
8–1	1·46	0·07			
2′–3′	1·61	0·08	3–8	3·21	0·08
3′–4′	1·61	0·12	4–7	3·14	0·08
4′–5′	1·58	0·10	3′–8′	2·95	0·09
6′–7′	1·50	0·07	4′–7′	3·27	0·11
7′–8′	1·36	0·08		3·14	0·14
8′–1′	1·48	0·08			
	1·52	0·09			

Angles A–B–C

A–B–C	$\angle(A$–B–$C)$	$\sigma(\angle(A$–B–$C))$
1–2–3	132	4
4–5–6	118	5
5–6–7	125	4
8–1–2	117	4
1′–2′–3′	119	5
4′–5′–6′	123	5
5′–6′–7′	130	5
8′–1′–2′	122	5
	123	6
2–3–4	105	5
3–4–5	125	5
6–7–8	110	4
7–8–1	118	5
2′–3′–4′	113	5
3′–4′–5′	116	7
6′–7′–8′	106	5
7′–8′–1′	133	5
	116	10
Cl′–Rh–Cl	85·3	0·4
Cl′–Rh′–Cl	84·7	0·4
Rh–Cl–Rh′	94·4	0·5
Rh–Cl′–Rh′	94·5	0·5

and 2·38 found by Dahl *et al.* (1961) in $(RhCl(CO)_2)_2$. The Rh–Rh distance of 3·498 ± 0·005 Å may be compared with that of 3·31 Å in the carbonyl and with a Pd–Pd distance of 3·46 Å in (styrene–$PdCl_2$)$_2$ (Holden & Baenziger, 1955) and in $(EtPdCl_2)_2$ (Dempsey & Baenziger, 1955). The double-bond center to rhodium distance of 2·00 ± 0·04 Å compares well with the double-bond center to palladium distance of 2·04 Å in norbornadiene dichloropalladium (II) (Baenziger *et al.*, 1961).

Even though account has been taken of the anisotropic nature of the heavy atom vibrations the ring geometry is not well defined. The single bonds cannot be distinguished from the 'double' bonds on the basis of length. On the basis of their positions relative to the rhodium atoms they can be. The twelve single bonds average 1·52 ± 0·09 Å, with no individual significant variations (5% level) from this mean. The four double bonds average 1·44 ± 0·07 Å with no significant variations. This value may be compared with 1·46 ± 0·04 Å in norbornadiene dichloro-palladium (II) and with 1·43 ± 0·15 Å in (styrene–$PdCl_2$)$_2$ (Baenziger *et al.*, 1961). The 95% fiducial limits for this mean and standard deviation are 1·35 and 1·53 Å, and so there is about a 2% chance that the mean of 1·44 Å with a standard deviation of 0·07 Å, based on a sample size of four, can be from a normal population whose mean is 1·34 Å, the normal double-bond length. It is thus likely that the double bonds in 1,5-*cyclo*octadiene have lengthened upon being bonded to the rhodium atom.

A comparison of the infrared spectrum of $(RhCl(C_8H_{12}))_2$ with that of 1,5-*cyclo*octadiene provides corroborative evidence for a weaker double-bond in the complex. A band at 1657 cm.$^{-1}$, which occurs in the spectrum of 1,5-*cyclo*octadiene and which is associated with C=C stretching, does not occur in the spectrum of the complex at a frequency higher than 1475 cm.$^{-1}$, where the methylene deformation band occurs. We were unable to identify the C=C stretching band in the spectrum of the complex, and it is possible that it occurs at a frequency considerably lower than 1475 cm.$^{-1}$.* Notable among other differences between the spectra is a shift in the frequency of the olefinic hydrogen out-of-plane bending mode. In the spectra of 1,5 *cyclo*octadiene and of most other *cis*-olefins this mode appears as a strong infrared band near 675 cm.$^{-1}$. In the complex this band is displaced to higher frequencies (> 775 cm.$^{-1}$) toward the region of hydrogen bending frequencies in saturated molecules (> 1000 cm.$^{-1}$).

Unfortunately it is not possible, on the basis of the infrared data, to estimate with confidence the extent of the lengthening of the double bonds in the complex. There is about a 95% chance that the double bond mean is less than the single bond mean, that is, that the double bonds and single bonds are from different populations. Moreover, there is about a 95% chance that the C=C–C angle is greater than the C–C–C

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* For comparison a C–C single bond stretching frequency is in the region 1100–1000 cm.$^{-1}$.

angle. It seems likely then that the 'double' bonds in the complex are intermediate in length to a normal single and a normal double bond.

We feel that we have obtained all of the information on the ring geometry which is possible with the present visual intensity data. We agree with Baenziger *et al.* (1961) that in this type of problem better data are probably required if significant information on ring geometry is to be obtained.

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The Crystal Structure of Iron Pentacarbonyl

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Iron pentacarbonyl at −80 °C. is monoclinic, probably *Cc*, with

$$a=11\cdot71,\ b=6\cdot80,\ c=9\cdot28\ \text{Å};\ \beta=107\cdot6°;\ Z=4\ .$$

Intensities were collected for the three zones [010], [001], and [110] at temperatures ranging from −70 to −110 °C. The crystal structure was determined by heavy-atom methods, and refined with the aid of two-dimensional Fourier syntheses. The molecule has the expected form of a trigonal bipyramid, but is slightly distorted in such a way as to allow closer packing.

Introduction

Ewens & Lister (1939) have shown by electron-diffraction studies of the gas that the molecule of iron pentacarbonyl ($Fe(CO)_5$) has the form of a trigonal bipyramid. However, recent investigations in the Division of Pure Chemistry have made it desirable to confirm this important result by crystal-structure analysis.

Experimental details

Iron pentacarbonyl is a straw-coloured liquid which freezes at −20 °C. The X-ray data were obtained from precession and Weissenberg photographs taken at temperatures ranging from −70 to −110 °C. Distilled material was sealed in a thin-walled glass capillary of about 0·4 mm. diameter, and single crystals were grown by alternate slow freezing and partial melting of the sample. Suitable crystals were easy to grow, but when cooled to the working temperature they invariably split into two or more fragments. Sometimes the damage to the crystal was comparatively slight, and the photographs were usable. All the X-ray data have been obtained from such photographs. Mo $K\alpha$ radiation was used throughout.

The crystal data at −80 °C. (obtained from precession photographs) are