The Crystal Structure of Ruthenium Tetracarbonyldiiodide

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Crystals of $Ru(CO)_4I_2$ are monoclinic, space group $C2/c$,

$$a = 7.15 \pm 0.02, \quad b = 11.04 \pm 0.03, \quad c = 12.70 \pm 0.03 \text{ Å}; \quad \beta = 91.3 \pm 0.3°,$$

with four formula units per unit cell. Three-dimensional least-squares refinement of all atoms resulted in a final R value of 8.6%. The structure consists of discrete $Ru(CO)_4I_2$ molecules. The molecular unit of C_{2v}–$2mm$ symmetry is an octahedron of four carbonyls and two iodines; the iodines are *cis* to one another.

Introduction

Although extensive studies of the structural features of metal carbonyl halides have been carried out by infrared spectroscopy (Abel *et al.*, 1958; Abel & Wilkinson, 1959; Brimm *et al.*, 1954; Chatt *et al.*, 1960; Edgell, 1961; Hileman *et al.*, 1961*a, b*; Hinds, 1958; Irving, 1956; Irving & Magnusson, 1956, 1958; Wilson, 1958; Wilt, 1960; Yang & Garland, 1957), to date the structures of only two compounds, [Mn(CO)$_4$Br]$_2$ (Dahl, 1961; Dahl & Wei) and [Rh(CO)$_2$Cl]$_2$ (Dahl *et al.*, 1961), have been unambiguously determined by X-ray diffraction.

The present investigation of $Ru(CO)_4I_2$ is an outgrowth of our work on the ruthenium carbonyls (Corey & Dahl, 1961; Dahl *et al.*). Manchot & Manchot (1936) reported the preparation of three ruthenium carbonyls. Our first attempts to prepare these compounds by their general method yielded a new compound, $Ru(CO)_4I_2$ (Corey *et al.*, 1962). A molecular configuration for $Ru(CO)_4I_2$ was proposed from its infrared spectrum (Corey *et al.*, 1962) and subsequently confirmed by this X-ray work.

Experimental procedure

Golden yellow single crystals of $Ru(CO)_4I_2$ were prepared and isolated in our laboratory by Mr Eugene R. Corey (Corey *et al.*, 1962). A small crystal of dimensions $0.20 \times 0.13 \times 0.04$ mm. was chosen and used without absorption corrections. The lattice lengths were determined from precession photographs; β was determined from a Weissenberg photograph.

A total of 374 independent diffraction maxima were obtained with Zr-filtered Mo $K\alpha$ radiation for nine reciprocal layers, $h0l$ to $h8l$, by application of the usual Weissenberg multiple-film equi-inclination technique. Intensities of all observed spots were estimated

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visually by comparison with calibrated intensity strips. Timed-exposure precession photographs were taken for the $0kl$ and $hk0$ zones with Mo $K\alpha$ radiation; the precession intensity data corrected for Lorentz-polarization effects were used to initially place the corrected Weissenberg intensity data on a common scale.

Crystal data

$Ru(CO)_4I_2$; mol.wt. = 466.9; sublimes at 126 °C. Monoclinic, with

$$a = 7.15 \pm 0.02, \quad b = 11.04 \pm 0.03, \quad c = 12.70 \pm 0.03 \text{ Å};$$
$$\beta = 91.3 \pm 0.3°.$$

Volume of unit cell = 1.002 Å^3. Density: calculated = 3.09 g.cm.$^{-3}$; measured = 2.98 g.cm.$^{-3}$. Four molecules per unit cell; total number of electrons per unit cell, $F(000) = 824$. Linear absorption coefficient for Mo $K\alpha$ radiation, 82 cm.$^{-1}$. Systematic absences: hkl for $h+k$ odd; $h0l$ for l odd. Probable space group: either $Cc(C_s^4)$ or $C2/c(C_{2h}^6)$. The final space group chosen, $C2/c$, was determined by the structure ultimately found.

Determination of the structure

Two-dimensional Patterson projections were calculated for the three principal zones. Interpretation of these projections yielded a trial structure consistent with the space group $C2/c$; the four ruthenium atoms are located on two-fold axes corresponding to one set of four-fold special positions $(4e)$, and the eight iodines occupy the general eight-fold set of positions $(8f)$ (*International Tables for X-ray Crystallography*, 1952). These positions are as follows:

$8f$ $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + x, y, z; \ \bar{x}, \bar{y}, \bar{z}; \ \bar{x}, y, \frac{1}{2} - z;$
$\quad x, \bar{y}, \frac{1}{2} + z.$

$4e$ $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + 0, y, \frac{1}{4}; \ 0, \bar{y}, \frac{3}{4}.$

The parameters obtained were refined by least-squares on an IBM 650 computer (Senko & Templeton, 1956)

with individual isotropic thermal parameters and constant weighting. A discrepancy factor

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o| \times 100$$

of 13·5% was obtained for this refinement of ruthenium and iodine atoms only.

Fig. 1. A composite of contour sections of a three-dimensional partial-difference electron-density synthesis showing the two asymmetric carbonyl groups in one molecule. The positions of the ruthenium and iodine atoms, which are subtracted out, are indicated. Contours are at intervals of 1 e.Å^{-3} with lowest contour at 1 e.Å^{-3}.

The carbon and oxygen positions then were obtained from a three-dimensional partial-difference Fourier synthesis in which the coefficients ΔF were calculated by subtraction of the temperature-corrected structure factors, F_c', corresponding to the contributions of the Ru and I atoms, from the observed structure factors (i.e., $\Delta F = F_o - F_c'$). This synthesis clearly revealed the positions of the carbon and oxygen atoms. Fig. 1 shows the superimposed contoured sections parallel to (010) corresponding to the two asymmetric carbonyl groups of one molecule and indicates the resolution of these light atoms obtained in this heavy atom problem.

Refinement of the structure on an IBM 704 computer with a full matrix least-squares program (Busing & Levy, 1959) resulted in a final discrepancy factor $R = 8·6\%$ for the 374 observed Weissenberg reflections. The refinement again was based on individual isotropic thermal parameters, but variable weights (Hughes, 1941; Lavine & Lipscomb, 1954) were assigned to the observed structure factors according to the functions $\sqrt{w} = 10/F_o$ if $F_o > 4F_{min}$; $\sqrt{w} = F_o/1·6F^2_{min}$ if $F_o \leq 4F_{min}$. For ruthenium and iodine the scattering factors used were those of Thomas & Umeda (1957); for carbon and oxygen the values used were those of Berghuis et al. (1955).

Table 1. Observed and calculated structure factors

The observed and calculated structure factors are compared in Table 1. Table 2 gives the final positional and thermal parameters together with their standard deviations.

Discussion of the structure

The structure is made up of discrete Ru(CO)$_4$I$_2$ molecules. The molecular unit can be described as a slightly distorted octahedron with four carbonyls and two iodine atoms surrounding a central ruthenium atom; the iodines are cis to one another. Within limits of accuracy imposed by the standard deviations, the molecular point group symmetry of the molecules is C_{2v}–$2mm$; only the two-fold axis is required by the space group. This cis-octahedral molecular arrangement is consistent with the infrared spectrum of the

Table 2. Final positional and thermal parameters with standard deviations

Position		x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B
8f	I	−0·1564	0·1586	0·3757	0·0004	0·0004	0·0002	3·7 ± 0·1
4e	Ru	0·0	−0·0110	0·2500	—	0·0005	—	2·5 ± 0·1
4e	C$_1$	0·230	−0·001	0·342	0·007	0·005	0·004	3·8 ± 0·9
4e	O$_1$	0·355	−0·010	0·384	0·004	0·005	0·003	3·8 ± 1·3
4e	C$_2$	0·119	−0·137	0·157	0·007	0·006	0·004	4·3 ± 1·1
4e	O$_2$	0·180	−0·192	0·099	0·005	0·005	0·004	5·8 ± 1·1

compound (Corey *et al.*, 1962) and is in agreement with the *cis*-octahedral configuration proposed for the homologue, $Fe(CO)_4I_2$, on the basis of dipole moment studies (Hieber & Weiss, 1956).

Table 3. *Intramolecular distances and angles with standard deviations*

Distances (Å)		Bond angles	
Ru–I	$2\cdot719 \pm 0\cdot007$	I–Ru–I'	$92\cdot9 \pm 0\cdot3$
Ru–C_1	$2\cdot00 \pm 0\cdot05$	C_1–Ru–I	$87\cdot7 \pm 1\cdot4$
Ru–C_2	$2\cdot02 \pm 0\cdot06$	C_2–Ru–I'	$86\cdot8 \pm 1\cdot7$
C_1–O_1	$1\cdot03 \pm 0\cdot05$	C_2–Ru–C_2'	$93\cdot4 \pm 3\cdot3$
C_2–O_2	$1\cdot06 \pm 0\cdot07$	C_1–Ru–I'	$87\cdot8 \pm 1\cdot4$
Ru $\cdots O_1$	$3\cdot02 \pm 0\cdot04$	C_1–Ru–C_2'	$92\cdot8 \pm 1\cdot9$
Ru $\cdots O_2$	$3\cdot07 \pm 0\cdot05$	C_2–Ru–I	$179\cdot3 \pm 1\cdot3$
$I_1 \cdots I_2$	$3\cdot94 \pm 0\cdot01$	O_2–C_2–Ru	$170\cdot8 \pm 5\cdot0$
		O_1–C_1–Ru	$169\cdot8 \pm 5\cdot2$

Average standard deviations in coordinates were found to be $0\cdot0055$ Å for ruthenium (i.e., along the two-fold axis), $0\cdot0033$ Å for iodine, $0\cdot054$ Å for carbon, and $0\cdot044$ Å for oxygen atoms. Table 3 lists intramolecular distances and angles with their standard deviations. The Ru–I distance is $2\cdot72$ Å (e.s.d. $0\cdot007$ Å); the average Ru–C and C–O bond lengths of $2\cdot01$ Å (e.s.d. $0\cdot06$ Å) and $1\cdot04_5$ Å (e.s.d. $0\cdot06$ Å) respectively are not known with sufficient accuracy to permit meaningful comparisons with other metal carbonyl bond lengths. The ligand–metal–ligand bond angles do not differ appreciably from those of a regular octahedron. Fig. 2 shows a molecule of $Ru(CO)_4I_2$.
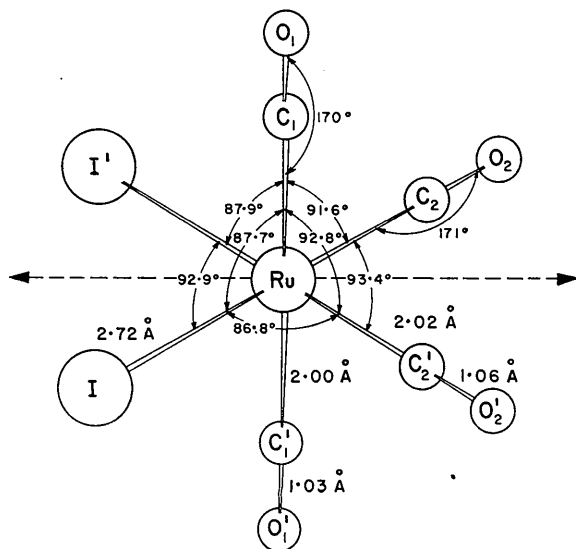
Fig. 2. The molecular configuration of $Ru(CO)_4I_2$.

Figs. 3 and 4 show the [100] and [010] projections of the Unit Cell respectively and clearly indicate the packing in the molecular crystal. If the two-fold axis of $Ru(CO)_4I_2$ crystallographically oriented in the **b** direction is assumed to be along the molecular [$\bar{1}10$] direction, the [111] direction of each idealized octahedral molecule approximately coincides with the

c axis. The centers of the molecules (i.e., ruthenium atoms) lie in rows along **c** which are located at $x=0$, $y=0$ and $x=\frac{1}{2}$, $y=\frac{1}{2}$. All octahedra are similarly oriented except that in a given row the iodines on adjacent octahedra are on opposite edges (see Fig. 3). Minimum intermolecular distances are $3\cdot31$ Å for $O \cdots O$ contacts, $3\cdot50$ Å for $I \cdots O$ contacts, and $3\cdot53$ Å for $C \cdots O$ contacts.
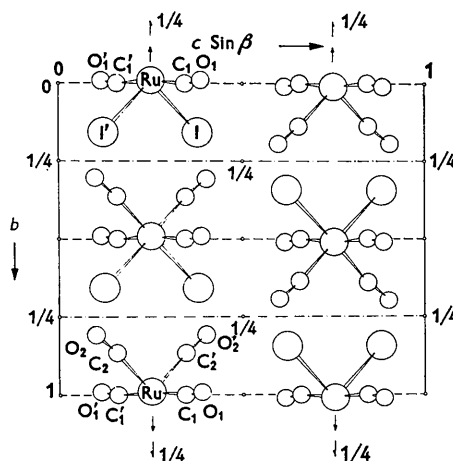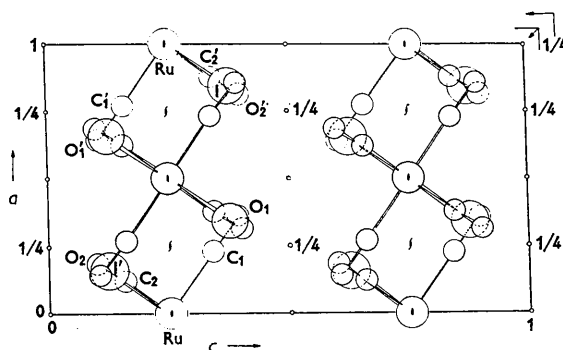

Fig. 3. [100] projection of the unit cell.

Fig. 4. [010] projection of the unit cell.

The preference of strongly π-bonding carbonyl groups for low metal valency states in transition metal carbonyl complexes (Hieber, 1948; Hieber, 1952; Coates, 1961; Pauson, 1960; Nyholm, 1961) is illustrated by the stability of the Ru(II) valency state in $Ru(CO)_4I_2$ and in the corresponding complexes $RuL_2(CO)_2I_2$, where L is a monodentate ligand with an unshared pair of electrons available for σ-bonding and with possible π-bonding capacity, e.g., nitrogen bases and derivatives of phosphines, arsines, and stibines (Irving, 1956; Hieber & Heusinger, 1956; Emelius & Anderson, 1960). Of course, some delocalization of charge on the metal is obtained by the utilization of the *d*-orbital electrons of the metal in π-bonding with the empty antibonding CO π-type orbitals. It should be noted that $Ru(CO)_4I_2$ obeys the 'inert-gas rule' which essentially means that all the low-energy

bonding orbitals of the metal are utilized at least to some extent in stabilizing the molecule.

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A Note On Self Consistent Bond Lengths for Tetracene and Pentacene

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Approximate self-consistent bond lengths have been calculated for tetracene and pentacene. The agreement with recent experimental results, obtained from X-ray crystallography, is reasonable.

Method and results

Brown & Bassett (1958) have described a very quick method for determining the first-order eigenvector when a perturbation is applied to a system which has a real symmetric Hamiltonian matrix. Subsequently, Coulson & Gołebiewski (1961) have applied Brown & Bassett's result in the development of a simple and approximately self-consistent method for calculating the bond lengths of conjugated systems.