A Structural Study of

Rhodium Carbonyl Chloride and

Rhodium Carbonyl Bromide

by

John Robert Wilt

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Signature of Author

Signature redacted

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Certified by

Signature redacted

Thesis Supervisor

Accepted by

Signature redacted

Head, Department of Chemistry

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Abstract

Rhodium carbonyl chloride, $Rh_2Cl_2(CO)_4$, and rhodium carbonyl bromide, $Rh_2Br_2(CO)_4$, are discussed from a structural point of view. Both were found to be dia-magnetic and to possess dipole moments. Infrared spectra of solutions are presented for the NaCl and KBr regions; a high resolution grating instrument was used to study the carbonyl stretching region. Gas spectra are pre-sented also. Only vibrational bands due to CO motions were observed and these showed that both complexes have the same structure.
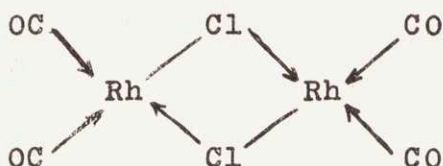
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FIGURE GUIDE

I. Introduction

Rhodium carbonyl chloride, bromide, and iodide were first discussed by Heiber.[1,2] In these works he discussed the preparation of these complexes and established the general formula $Rh_2X_2(CO)_4$ (X=Cl,Br, or I), and proposed the following structure for the chloride complex:

Structure I

This structure was also presented by Vallerino[3] in a discussion concerned primarily with other rhodium complexes derived from these.

Another structure for rhodium carbonyl chloride was proposed by Garland and Yang,[4] and again by Hinds.[5] This structure is as follows:
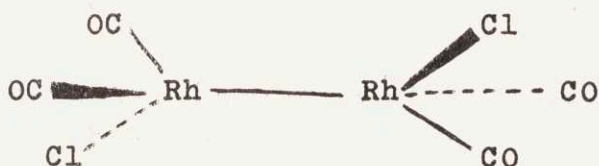
Structure II

The questions which precipitated this work were two: (a) do the chloride comples and the bromide complex have the same structure? and (b) what are the structures?

II. Experimental

A. Preparation of $Rh_2Cl_2(CO)_4$

The method used was that of Heiber and Lagally.[1]

Hydrated rhodium trichloride[6], $RhCl_3 \cdot xH_2O$ (1.1 g, 0.0052 mole), was placed in a U-shaped reaction tube at room temperature. The outlet from the system was connected to a butyl phthalate bubbler. The system was flushed with chemically pure carbon monoxide,[7] the flow rate reduced to 10-15 bubbles of CO per minute, and the bottom part of the tube heated to 120-125° for 16 hours, the complex subliming into the upper (cool) part of the tube.

Yield: 0.60 g. (0.0015 mole) $Rh_2Cl_2(CO)_4$, 60 % calculated on the basis of 1.1 g $RhCl_3$.

B. Preparation of $Rh_2Br_2(CO)_4$

The method used was also that of Heiber and Lagally.[1] This preparation was done a number of times; the general procedure is outlined below.

The rhodium was precipitated quantitatively as the yellow hydroxide from solutions of $RhCl_3$ in $NaHCO_3$ (100 % xs) on digesting for 12 hours at 95°. The precipitate was filtered by suction and washed with water, then dissolved in dilute HBr (50 % xs) by digesting 4 hours at 95°. The solution was evaporated until the solute was sticky (not dry), and the crude $RhBr_3$ dissolved in dry methanol. The solution was filtered by gravity, the precipitate washed with dry methanol and discarded. The solution was evaporated until the product seemed dry, but was not heated above 90°. The $RhBr_3 \cdot xMeOH$ was loaded in lots of about 2 g. into an improved reaction tube which permitted

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the CO to enter from the bottom and the complex to condense
in a bent portion vertically above the CO inlet. The CO
was saturated with MeOH before it entered the reaction tube
and the outlet from the system connected to a butyl phthalate
bubbler as before. The system was flushed with CO and the
flow rate reduced to 10-15 bubbles per minute. The lower
part of the reaction tube was heated at 80-85° for 7-10
days, then at 140-150° for 24 hours. Overall yields
ranged from 30-50 % calculated on the basis of $RhCl_3$.

C. Magnetic Susceptibility

Measurements were made on a Gouy balance[8] which is
described in detail elsewhere.[9] Gouy tubes were constructed
of 4 mm. (O.D.) pyrex glass tubing and 7/25 standard taper
joints. No correction was made for the diamagnetism of the
glass. The tubes were filled to a depth of about three inches.
Both the chloride and bromide complexes were diamagnetic.

D. Dipole Moment

The technique used was the heterodyne-beat method,
which is fully described in reference 10. The specific
components of the apparatus were a General Radio Co. hetero-
dyne beat-frequency oscillator (G.R. type 1904-B), a General
Radio Co. precision air capacitor (G.R. type 722-D, range
10-1150$\mu\mu$f), a Heath Co. oscilloscope, a Hewlett-Packard
audio oscillator (H.P. model 200CR) and a small variable
radio capacitor (range 5-50$\mu\mu$f). The R. F. frequency
used was about 200 kc. The beat frequencies used were

about 30 kc for solution measurements and about 9.8 kc. for

air measurements. Density measurements were made using a

10 cc. pyncnometer. Refractive indices were measured on an

Abbe type refractometer manufactured by Bausch and Lomb Op-

tical Co. The data are collected in tables I and II and

are presented graphically in figures 1, 2, 3 and 4. The

slopes from the graphs are tabulated in table III. In

the plot of figure 4 the points fall on a curve which becomes

a straight line for mole fractions > 0.0003. This was shown

to be a property of the solute-solvent pair rather than due

to temperature variation within the instrument by measuring

the refractive index of the solvent at 25.1°. The value

obtained was $n_D^{25.1} = 1.393096 \pm 0.00006$ a.d., $(n_D^{25.1})^2 = 1.9349$.

This showed that the temperature variation within the instru-

ment would have to have been greater than 1°, which is

extremely difficult to imagine. For purposes of the cal-

culation the straight line was extrapolated to infinite dilu-

tion ($X_2 = 0$) and the value of $(n_D^{24.8})^2$ at the intercept

used.

The calculation of the dipole moment was performed us-

ing a method outlined in reference 12. After transforming

weight fractions to mole fractions the following relations

are obtained:

$$\infty(_0 P_2) = \frac{3 M_2}{\mathcal{S}_1} \left[\frac{\frac{d \epsilon}{d X_2}}{(\epsilon_1 + 2)^2} - \frac{\frac{d (n_D)^2}{d X_2}}{(n_{D_1}^2 + 2)^2} \right] \qquad (1)$$

$$\mu_2 = 0.0128 \times 10^{-18} \left[\infty(_0 P_2) T \right]^{\frac{1}{2}} \qquad (2)$$

Table I

Dipole moment data[11] for $Rh_2Cl_2(CO)_4$
Solvent - benzene   Temperature - $25°$

Mole Fraction $Rh_2Cl_2(CO)_4$ (X_2)	Density (ρ)	Refractive Index (n_D^{25})	$(n_D^{25})^2$	Dielectric Constant (ϵ)
0	0.8737	1.4981	2.2443	2.273±0.002 a.d.
0.00435	0.8858	1.4986	2.2457	2.284 "
0.00604	0.8900	1.4992	2.2476	2.296 "
0.00879	0.8976	1.4996	2.2487	2.308 "
0.01110	0.9032	1.5004	2.2512	2.320 "

Table II

Dipole moment data for $Rh_2Br_2(CO)_4$
### Solvent - isooctane   Temperature - $25°$ except $n^{24.8}$

Mole Fraction $Rh_2Br_2(CO)_4$	Density (ρ)	Refractive Index $(n_D^{24.8})$	$(n_D^{24.8})^2$	Dielectric Constant (ϵ)
0	0.6877	1.39063	1.9339	1.936±0.002 a.d.
0.002004	0.6910	1.39178	1.9371	1.944 "
0.003233	0.6956	1.39232	1.9386	1.951 "
0.005345	0.7028	1.39280	1.9399	1.953 "
0.007482	0.7048	1.39328	1.9412	1.960 "
0.01426	0.7247	1.39443	1.9444	1.989 "

Table III

Dipole moment data for $Rh_2Cl_2(CO)_4$ and $Rh_2Br_2(CO)_4$

Complex	$\frac{d\epsilon}{dX_2}$	Figure no.	$\frac{d(n_D)^2}{dX_2}$	Figure no.	$(n_D)^2$ intercept
$Rh_2Cl_2(CO)_4$	4.24	6	0.513	8	2.2443
$Rh_2Br_2(CO)_4$	3.69	7	0.517	9	1.9375

Dielectric constant versus mole fraction $Rh_2Cl_2(CO)_4$ — figure 1
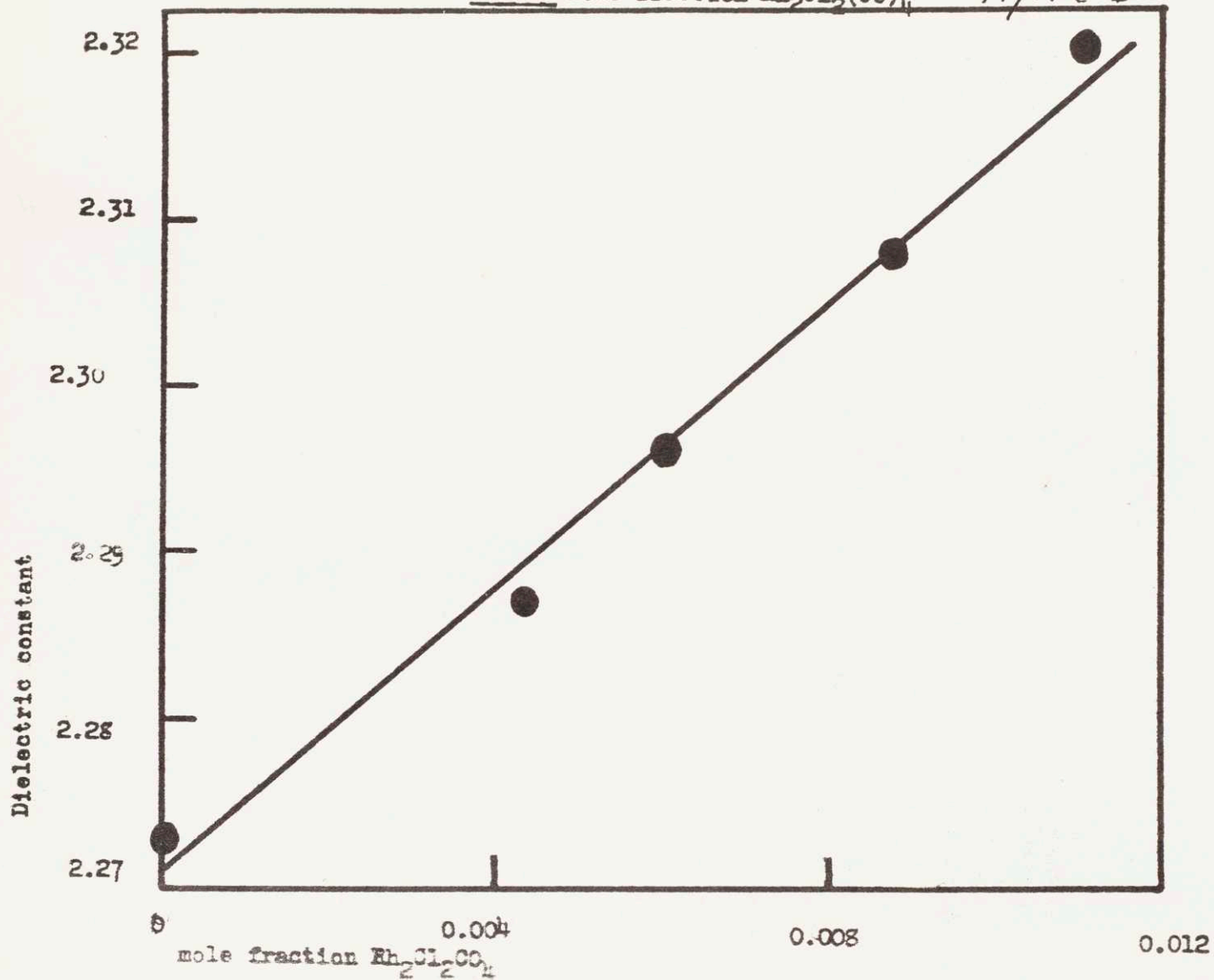
Index of refraction versus mole fraction $Rh_2Cl_2(CO)_4$ — figure 2

Dielectric constant versus mole fraction Rh$_2$Br$_2$(CO)$_4$ figure 3
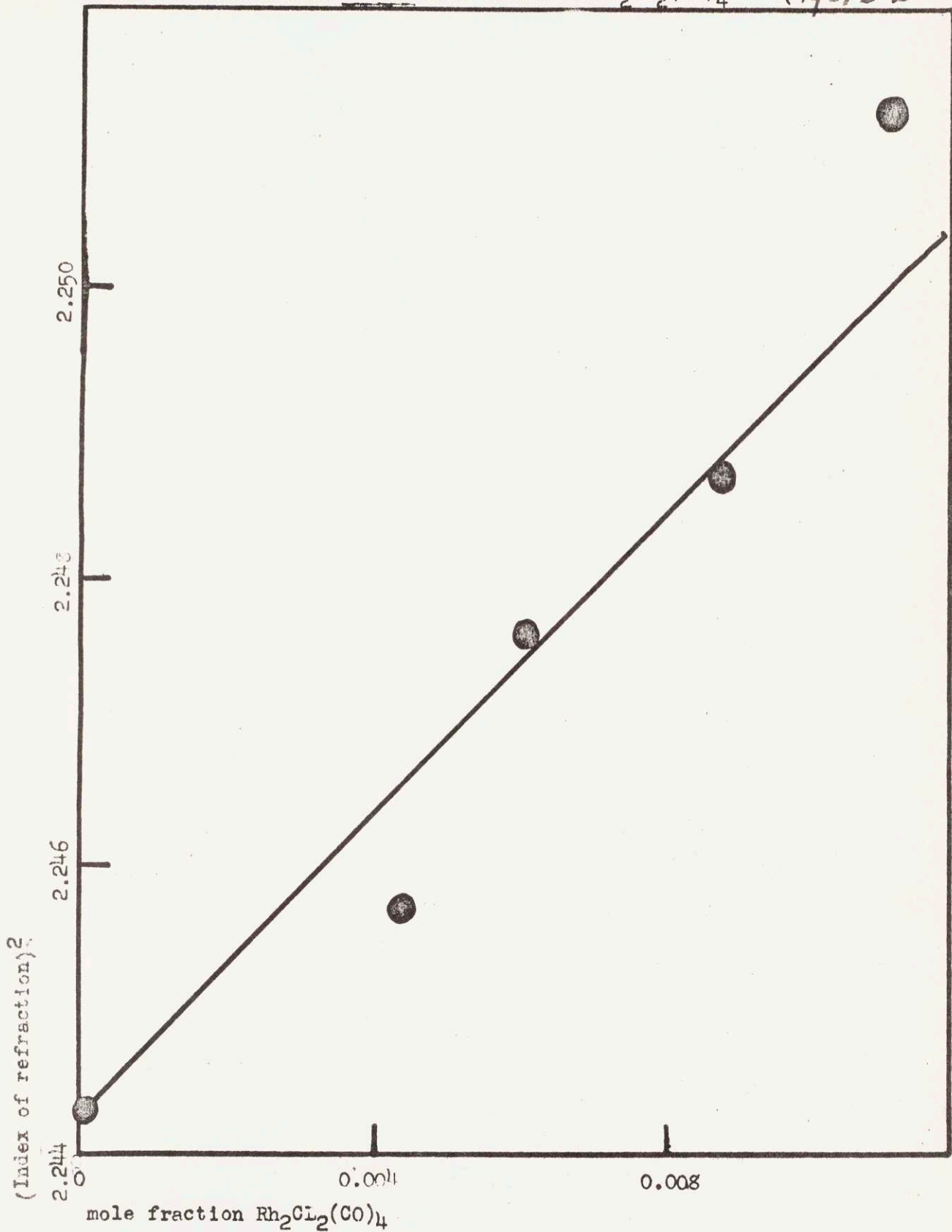
mole fraction Rh$_2$Br$_2$(CC)$_4$
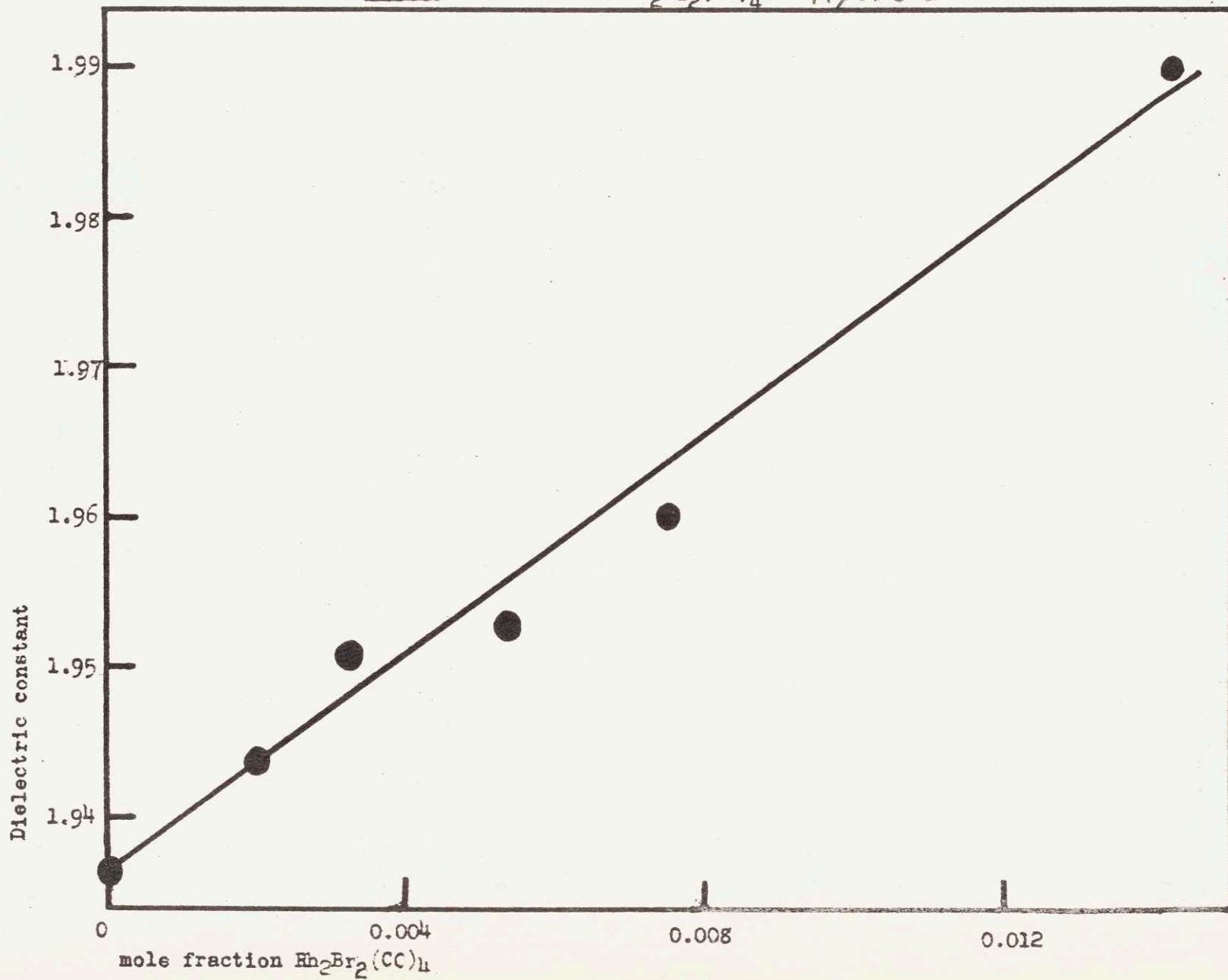
(Index of refraction)^2 versus mole fraction $Rh_2Br_2(CO)_4$ figure 4

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(Index of refraction)^2

1.944

1.942

1.940

1.938

1.936

1.934

0   0.004   0.008   0.012

mole fraction $Rh_2Br_2(CO)_4$

where $_\infty(_0P_2)$ is the orientation polarization at infinite
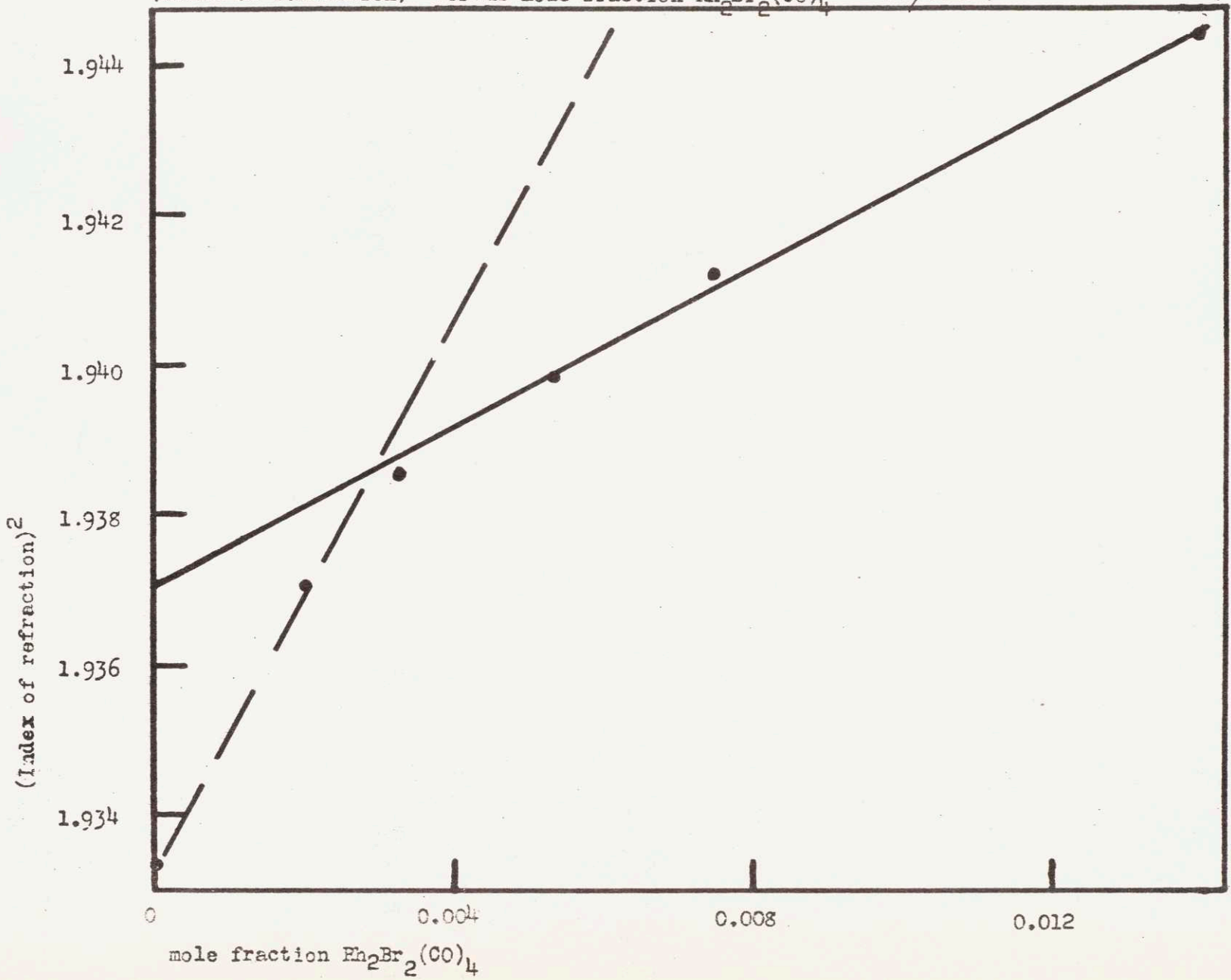dilution, M is the molecular weight, $\int$ is density, μ dielec-
tric constant, n_0 index of refraction, T is absolute temper-
ature, and the subscripts 1 and 2 refer to solvent and sol-
ute, respectively.

Using the data from tables I, II, and III in equations
(1) and (2) the following values are obtained for the di-
pole moments:

$$Rh_2Cl_2(CO)_4 \qquad \mu = 1.64 \qquad 0.3 \text{ Debye}$$

$$Rh_2Br_2(CO)_4 \qquad \mu = 2.23 \qquad 0.3 \text{ Debye}$$

E. Infrared Spectra

Spectra were recorded in the NaCl region (5000 - 640
cm^{-1}) and in the KBr region (840 - 390 cm^{-1}) on a stan-
dard Baird-Atomic spectrophotometer. Detailed study of the
carbonyl stretching region (2200 - 1600 cm^{-1}) was possible
through the use of a Perkin-Elmer model 12 spectrophotome-
ter modified for use with a grating.[13] Spectra in the NaCl
region showed that the carbonyl stretching bands were the
only ones present in this region.

Spectra of both chloride and bromide complexes were
recorded in saturated haxane solution (about 1 mole%)
using standard 0.1 mm. KBr microcells. These spectra are
shown in figures 5 and 6 (carbonyl stretching region) and
in figure 7 (KBr region). Exact band positions are tabulated
in table IV. Spectra of both chloride and bromide complexes

Spectrum of $Rh_2Cl_2(CO)_4$ in n-hexane   figure 5

per cent transmission

wavelength (cm⁻¹)

11
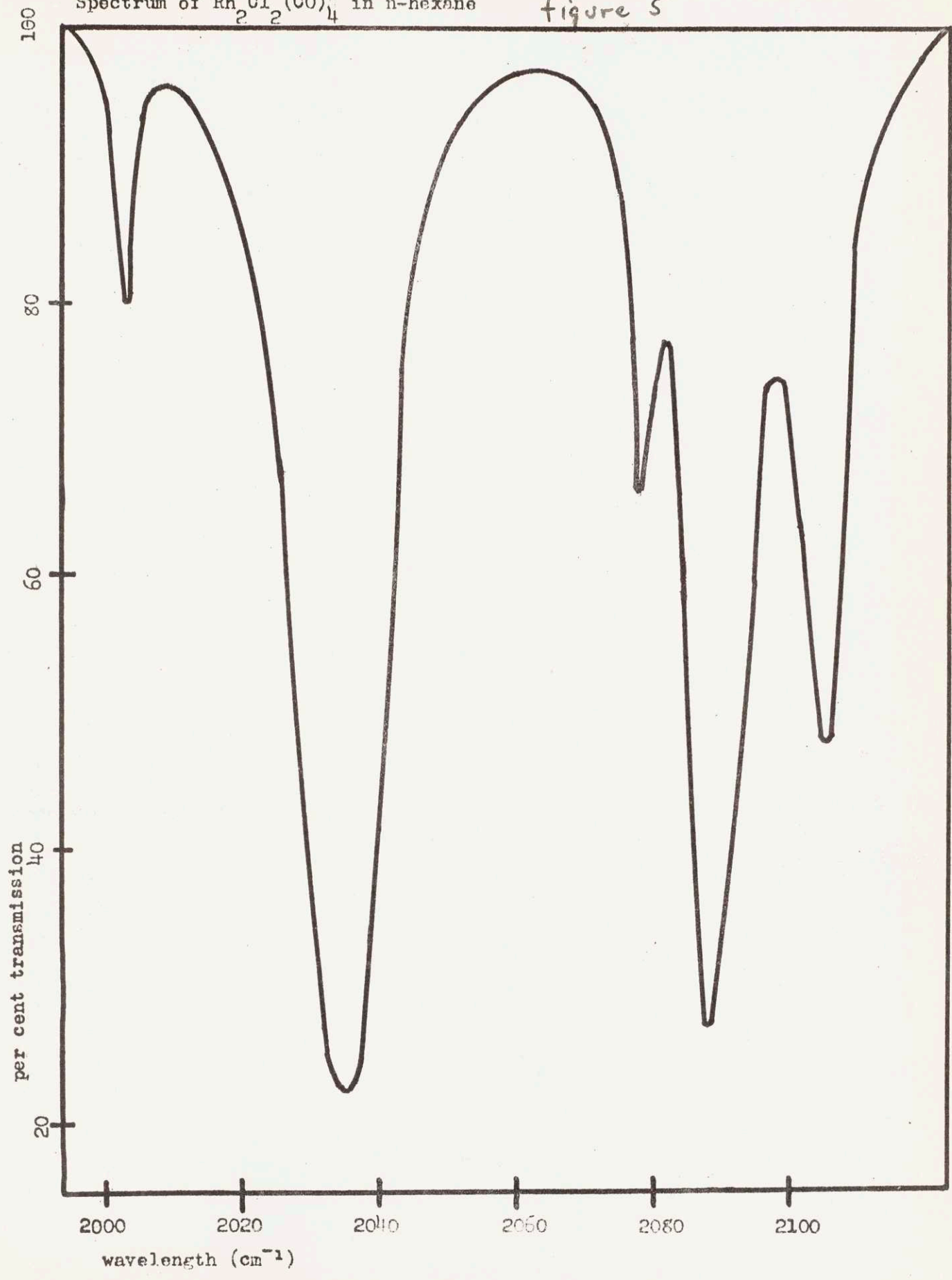
Spectrum of $Rh_2Br_2(CO)_4$ in n-hexane   figure 6

percent transmission

wavelength (cm^{-1})

12
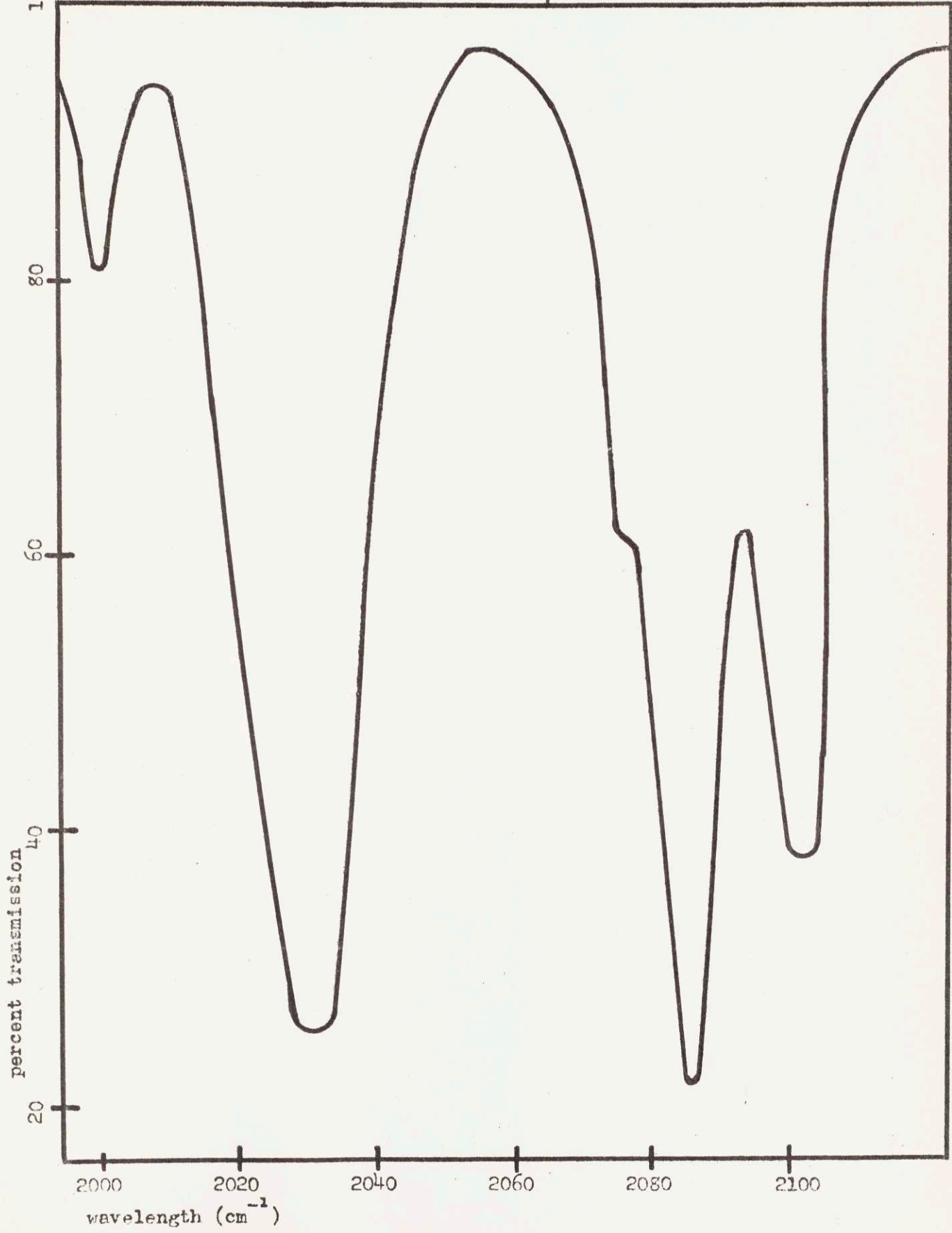
Spectra of $Rh_2Cl_2(CO)_4$ (top) and $Rh_2Br_2(CO)_4$ (bottom) in n-hexane   figure 7

per cent transmission

wavelength (microns).
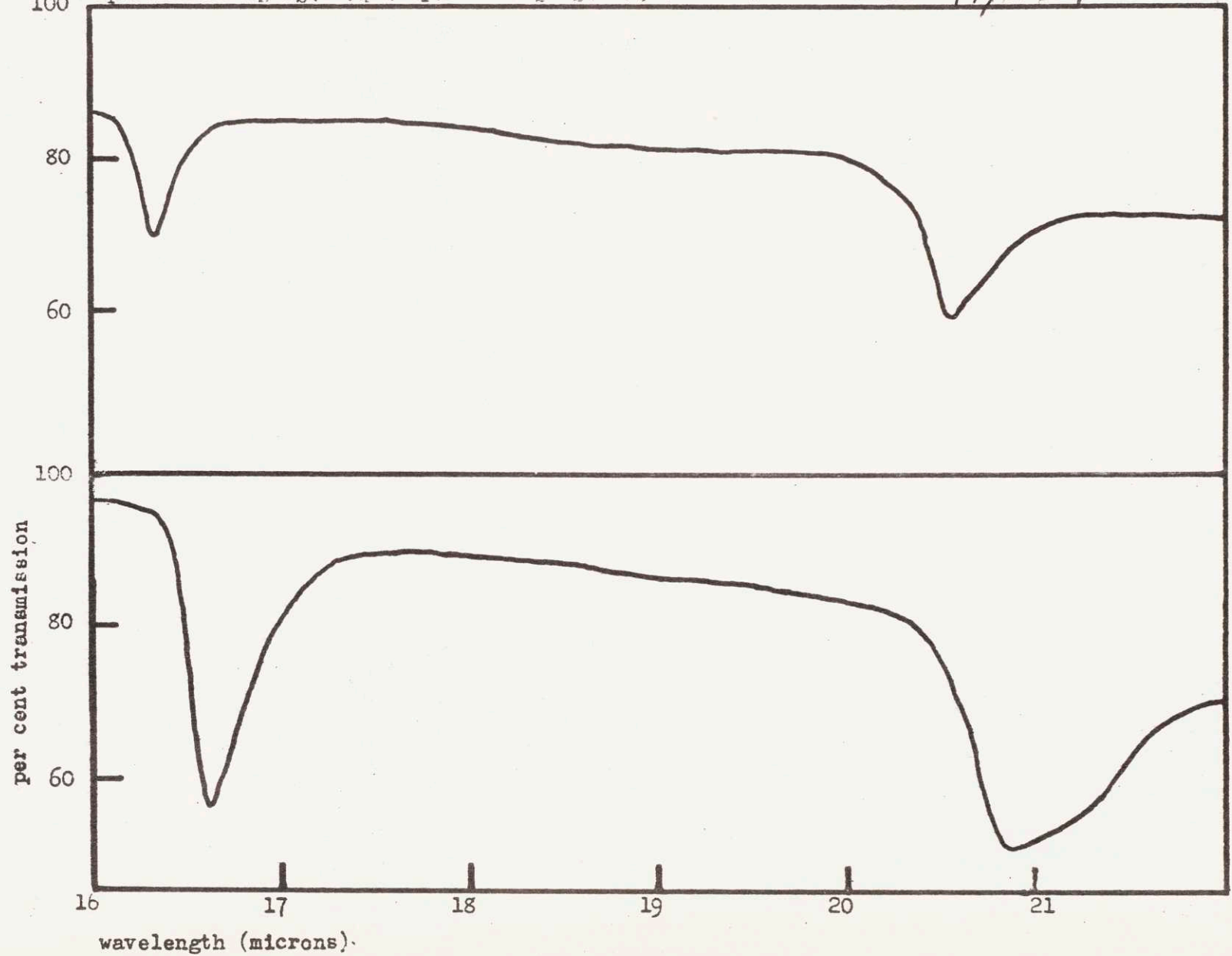
13

Spectrum of $Rh_2Cl_2(CO)_4$ (gas) figure 8

per cent transmission

wavelength (cm⁻¹)

14

Spectrum of $Rh_2Br_2(CO)_4$ (gas)   figure 9

Spectrum A 71°C   Spectrum B 113°C

15

Table IV

Infrared band positions for $Rh_2Cl_2(CO)_4$ and $Rh_2Br_2(CO)_4$

$Rh_2Cl_2(CO)_4$		$Rh_2Br_2(CO)_4$	
Solution	Gas	Solution	Gas
2105 cm^{-1} (m)	2107 cm^{-1} (vw)	2100 cm^{-1} (m)	2107 cm^{-1} (vw)
2089 " (vs)	2095 " (s)	2087 " (vs)	2092 " (s)
2079 " (vw)		2076 " (vw)	
2035 " (vs)	2043 " (s)	2032 " (vs)	2042 " (s)
2003 " (w)	2016 " (w)	2001 " (w)	2018 " (w)
610 " (m)		599 " (m)	
483 " (m)		475 " (m)	

Note: s-strong, m-medium, w-weak, v-very

in Nujol mulls could be superimposed on the corresponding spectra in hexane solution. Slit widths of 0.3 mm. were used on the model 12 for taking the solution spectra.

Spectra of both chloride and bromide complexes in the gas phase were recorded as a function of temperature in the range 25 - 160° C. Representative spectra are presented in figures 8 and 9 and exact band positions are tabulated in table IV. No bands were observed in the gas spectra of the KBr region. This cannot be construed as meaning that such bands do not exist, as no unambiguous method was devised to show that sufficient complex was in the beam to give bands. For details on the construction of the gas cell used and detailed procedures used in making measurements see appendix 1. Slit widths for taking gas spectra on the model 12 were about 0.6 mm.

III. Conclusions

The similarity in the infrared spectra of corresponding phases indicates very strongly that the two complexes $Rh_2Cl_2(CO)_4$ and $Rh_2Br_2(CO)_4$ have the same structure.

Any structure involving CO bridges is ruled out by the absence of infrared bands in the CO bridging region (1800 - 1900 cm^{-1}).

From the standpoint of structure I, only two fundamental CO stretching modes would be infrared active if the molecule has a center of symmetry. Also if the

structure has a center of symmetry the molecule could not have a dipole moment. It is possible, however, to write structures of the type of structure I which do not have a symmetry center. Since Miss Vallerino's work[3] seems to indicate that monomeric complexes derived from $Rh_2Cl_2(CO)_4$ have square planar configurations, one might picture two planar $RhCl(CO)_2$ groups which intersect along the Cl-Cl line with a dihedral angle not equal to $180°$. This structure does not have a center of symmetry, and thus has four infrared active CO stretching fundamentals, and has a dipole moment. Further, since in this structure the halogen contribution to the dipole moment is directed oppositely to that of the CO, one would expect the more covalently bonded bromide complex to have a greater net dipole moment than the more ionic chloride complex.

From the standpoint of structure II one expects four carbonyl stretching fundamentals. Further, if one considers only one of the $RhCl(CO)_2$ groups it is apparent that the resultant dipole moment is composed of oppositely directed components due to halogen and carbonyl. The dipole moment, therefore, is expected to be larger for the bromide than for the chloride in the monomer units. If one further postulates that the barrier to rotation about the Rh-Rh bond is about the same in bromide and chloride complexes, a larger net dipole moment would be expected for the bromide dimer than for the chloride.

Thus while it is possible to say that all the evidence
points to both complexes having the same structure,
it is not possible to say definitely what that structure is.
One can, however, rule out any structure having CO
bridges or having a center of symmetry. Future work
on the spectra at lower frequencies will be necessary
to a complete determination of structure.

Appendix 1

Construction and Use of a Gas Cell

A gas cell 10 cm. long was constructed of 41 mm. (O.D.) pyrex glass tubing. A stopcock was attached to the center of the cell by means of a ball and socket joint. A thermocouple was placed next to the glass on the outside of the cell near the center. The cell was wrapped with asbestos paper and a heating coil of Chromel resistance wire was placed over this paper. The cell was wrapped with another layer of asbestos paper and insulated with alternate layers of aluminum foil and asbestos cloth (two layers of each). The temperature was controlled with a Variac, the range being about 25 - 250° C. with a coil resistance of about 190 ohms.

The silver chloride windows (2 mm. thick) were attached with Araldite[14] type I thermal setting resin which was cured two hours at 200° (measured on the thermocouple).

Runs were made by placing about 0.2 g. complex in the cell and flushing the cell with dry nitrogen. Initially the cell was then filled with dry nitrogen to about 2/3 atmosphere and heated, but eventually the Araldite, which was the best of the adhesives tested,[15] failed. The final runs were made by filling the cell to 1 atmosphere with dry nitrogen, then heating.

Difficulties experienced were primarily fogging
of the AgCl windows, decomposition within the cell, and
the failure of the adhesive.

The Araldite failure was due in part to the lack of
structural strength of the windows. When heated under
vacuum the windows flexed in by as much as 3 mm.,
putting great strain on the adhesive. When the cell
was cooled under vacuum the windows sometimes cracked
off, at times cracking the glass around the window. This
occurred only on cooling the cell, and happened when
the cell was cooled very slowly as well as when it
was cooled more quickly. These leaks eventually became
irreparable, necessitating filling the cell to 1 atm.
with nitrogen and heating quickly, thus blowing the nitrogen
out the cracks while not allowing air to enter. On cooling,
of course, air was admitted to the cell, and the hot
complex immediately decomposed. This lack of tightness
in the cell was directly responsible for the inability
to show that sufficient complex was in the beam to give
gas spectra in the KBr region.

Decomposition on the glass surfaces (not on the
AgCl) occurred even when the cell was tight and well
flushed with nitrogen. Cause of this decomposition
is undetermined.

Fogging of the windows is a common failing of AgCl

cells. Even though the windows were protected with aluminum foil except during the actual recording of spectra, the windows became less and less transparent. This fogging required wide slits and this was responsible for the low resolution of the gas spectra recorded on the model 12.

In general this author feels that KBr windows, in spite of their sensitivity to temperature change, would be better in terms of time, data, and cost. The KBr could be sealed to the cell with red glyptal, which is sufficiently gas-tight, but lacks the strength to stand the flexing of the AgCl, and has the additional advantage of being soluble in acetone. Araldite resins are insoluble in all common non-oxidizing media. Windows sealed on with Araldite resins can be removed only by use of a hot wire, followed by abrasive polishing of the surfaces.

Footnotes and References

1. Heiber and Lagally, Z. Anorg. allge Chem., 251, 96 (1943).

2. Heiber and Hensinger, Angewante Chemie, 68, 678 (1956).

3. Vallerino, J. Chem. Soc., 1957, 2287.

4. Garland and Yang, J. Phys. Chem., 61, 1504 (1957).

5. Leonard de C. Hinds, S.B. Thesis, M.I.T., May 26, 1958.

6. Obtained from A.D. Makay Co., New York, N. Y.

7. Obtained from The Matheson Co., East Rutherford, N.J.

8. Loaned through the courtesy of Dr. F.A. Cotton, Associate
   Professor of Chemistry.

9. M. Douglas Meyers, Ph.D. Thesis, M.I.T., Sept. 14, 1959.

10. Daniels, Mathiews, and Wilson, Experimental Physical
Chemistry, Fifth Edition, McGraw-Hill, New York, 1956,
Experiments 45 and 46.

11. These data were obtained by Dr. John T. Yates, Jr.,
and have not been reported previously. It is presented
here as a matter of convenience for comparison.

12. R.J.W. LeFevre, Dipole Moments, Third Edition, John
Wiley and Sons, New York, 1953, p. 58, method C.

13. A 60° CaF_2 prism was used in conjunction with a
150 lines/mm. grating which replaced the Littrow mirror.
A more detailed discussion is given in John T. Yates, Jr.
Ph.D. Thesis, M.I.T., May 19, 1960.

14. CIBA Co., New York, N.Y. trademark

15. Others included Hysol Epoxi Patch, Houghton Laboratories
                    Araldite type 101, CIBA Co.
                    Red glyptal