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## Comparison of Chlorine-36 Exchange With $K_2ReCl_6$ and $Cs_2ReOCl_5$

JOE D. WOODS<sup>1</sup>, JOANN GRUCA, AND CARL M. PIETRZAK

*Abstract.*  $K_2ReCl_6$  (IV), after precipitation from solutions of  $HCl^{36}$  with nitron, contained no significant radioactivity.  $Cs_2ReOCl_5$  (V), insoluble in  $HCl$ , after suspension in methanol containing  $HCl^{36}$  and filtration was radioactive. An x-ray diffraction determination of the  $Cs_2ReOCl_5$  unit cell parameters and a microscopic estimation of the surface of the samples made possible the calculation of 83% exchange of the surface chlorine atoms. Results agree with the generalization that octohedral complexes with no vacant d orbitals are inert, whereas those with at least one vacant d orbital are labile.

$Cs_2ReOCl_5$  is a yellow-brown crystalline solid, insoluble in dilute  $HCl$ . X-ray diffraction determination gave hexagonal unit cell parameters of  $a=7.04\text{\AA}$  and  $c=10.9\text{\AA}$ .

The application of isotopic tracers has been fruitful in giving information of the liability of coordination compounds (1). Taube (2) classified octohedral complexes with vacant d orbitals as labile and those with no vacant d orbitals as inert. By placing the complex in an environment with radioactive atoms common to those in ligands, a measure of the liability then would be how rapidly the percent of exchange approaches that of equilibrium.

Potassium hexachlororhenate (IV) has no vacant d orbitals in its electron structure:  $5d^1 5d^1 5d^1 (5d^2 6s^1 6p^3)$ , therefore should be inert. The hexachlororhenate (IV)—chloride exchange system was first investigated by Jexowska, Trzebiatowska et al (3) who concluded that the exchange reaction, if any, is extremely small. Rhenium (V) has one vacant d orbital and should be labile:  $5d^1 5d^1 5d^0 (5d^2 6s^1 6p^3)$ . Preliminary experiments revealed that  $K_2ReOCl_5$  is difficult to prepare and maintain without disproportionation. Pietsch and Erich (4) found that  $K_2ReOCl_5$  rapidly changes to  $K_4(Re_2OCl_{10})$ . Preliminary experiments revealed that the cesium salt, however, is stable probably because of its insolubility in dilute  $HCl$ . For this reason the cesium salt was used for the Re (V) compound.

Since  $K_2ReCl_6$  is soluble, the exchange experiment could be carried out in radioactive chlorine tagged solution. However, since  $Cs_2ReOCl_5$  is insoluble, a measure of the exchange with the estimated number of chlorine atoms on the surface was made. This involved a determination of the unit cell parameters and a measurement of the surface of the samples used in the exchange experiment. Other studies of exchanges on surfaces of insoluble substances have been

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done. For example, Sweitzer and Whiting (5) studied the exchange of radioactive silver in solution with insoluble silver chloride.

PREPARATION OF COMPOUNDS AND ANALYSIS

$K_2ReCl_6$

The  $K_2ReCl_6$  was prepared by a standard method (6). A U. V. spectrum of the preparation matched the spectrum of standard  $K_2ReCl_6$  in dilute HCl solution.

$Cs_2ReOCl_5$

*Preparation:* A modified method by Colton (7) was used to prepare  $Cs_2ReCl_5$ . Approximately 1 g of  $ReCl_5$  was dissolved in 40 ml. concentrated HCl. The solution turned dark green, then brown-orange. A stream of oxygen was bubbled through the solution and solid CsCl was added. A dull-yellow precipitate formed which was washed with concentrated HCl until washings were colorless. After final washes with ethanol and ether the solid product was dried in a desiccator over calcium chloride. Because  $ReCl_5$  reacts with water vapour it was handled in a glove bag filled with nitrogen.

*Analysis of  $Cs_2ReOCl_5$ :* The yellow product reduced mercuric chloride and oxidized iodide. A quantitative spectrophotometric analysis of two weighed samples produced the expected concentration of  $ReO_4^-$  and  $ReO_2$  when disproportionation occurred according to the following:

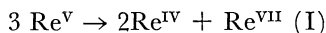


Table 1 gives results of the analysis.

Table 1. Spectrophotometric Analysis of the Disproportionation of the  $Cs_2ReOCl_5$

| Sample   | 1                      | 2                      |
|--|------------------------|------------------------|
| Wavelength, m $\mu$  | 238                    | 252                    |
| Extinction coefficient from a standard curve                                   | $3.23 \times 10^3$     | $1.58 \times 10^3$     |
| Concentration of $(ReO_4)^-$ calculated on application of the Beer-Lambert Law | $1.98 \times 10^{-4}M$ | $2.15 \times 10^{-4}M$ |
| Projected concentration of $Cs_2ReOCl_5$                                       | $5.94 \times 10^{-4}M$ | $6.45 \times 10^{-4}M$ |
| Concentration of $Cs_2ReOCl_5$ if sample was identical to this compound        | $6.02 \times 10^{-4}M$ | $6.64 \times 10^{-4}M$ |
| Per cent deviation between experimental and theoretical concentration values   | 2%                     | 3%                     |

*X-ray diffraction determination of unit cell parameters:* An x-ray powder diffraction pattern of the  $Cs_2ReOCl_5$  was carried out using a Debye-Sherrer camera of 114.6 mm. diameter with a filtered copper source ( $\lambda = 1.542 \text{ \AA}$ ) and ten hours exposure time. The diffraction data was treated by a method described by Cullity (8). Data for indexing the  $Cs_2ReOCl_5$  is shown in Table 2.

Table 2. X-ray Diffraction Data for Indexing the  $Cs_2ReOCl_5$ 

| Line | $S_{mm}$ | $\theta^\circ$ |
|------|----------|----------------|
| 1    | 15.3     | 7.7            |
| 2    | 25.0     | 12.5           |
| 3    | 29.2     | 14.6           |
| 4    | 30.5     | 15.2           |
| 5    | 35.4     | 17.7           |
| 6    | 38.6     | 19.3           |
| 7    | 43.6     | 21.8           |
| 8    | 46.4     | 23.2           |
| 9    | 50.9     | 25.4           |
| 10   | 53.1     | 26.6           |
| 11   | 57.3     | 28.6           |
| 12   | 60.2     | 30.1           |
| 13   | 63.3     | 31.6           |
| 14   | 65.3     | 32.6           |
| 15   | 69.1     | 34.6           |

For hexagonal crystals  $\sin^2\theta$  values are given by:

$$\sin^2\theta = A(h^2 + hk + k^2) + C l^2 \quad (\text{II})$$

where  $A = \frac{2}{3}a^2$  and  $C = \frac{2}{4}c^2$ .

$h, k, l$  = miller indexes for the particular line

$a, c$  = lattice constants

$\lambda$  = characteristic x-ray wave length

Assuming a hexagonal system permissible ( $h^2 + hk + k^2$ ) values of 1, 3, 4, 7, etc. were tabulated. Analysis of the data gave a value of  $A = 0.016$ , and  $C = 0.005$ , thus giving lattice parameters of  $a = 7.04\text{\AA}$  and  $c = 10.9\text{\AA}$ . Previous workers had qualitatively identified the lattice of the isomorphous  $K_2ReOCl_5$  as rhombohedral (9).

*Determination of density of compound:* The density of the  $Cs_2ReOCl_5$  crystals was determined from knowledge of the unit cell parameters, using the following:

$$\text{Density} = \frac{(M)}{(N)} \frac{(A)}{(V)} \quad \text{(III)}$$

where M = gram molecular weight,

N = Avogadro's number

A = number of molecules per unit cell

V = volume of unit cell.

The volume (V) of the unit cell is calculated from the parameters to be  $4.68 \times 10^{-22} \text{cm}^3$ . The number of molecules per unit cell is 2. Therefore, using the above equation for density, the density of  $\text{Cs}_2\text{ReOCl}_5$  was estimated to be  $4.58 \text{ g/cm}^3$ . This value is in accord with densities of similar compounds,  $\text{ReCl}_5$ ,  $4.9 \text{ g/cc}$ ;  $\text{KReO}_4$ ,  $4.8 \text{ g/cc}$ .

*Estimate of surface of samples:* The surface was estimated by measuring the particle sizes of a sample suspended in methanol using direct microscopic examination according to a method described by Chamot and Mason (10). Inspection of the particles of  $\text{Cs}_2\text{ReOCl}_5$  under 970X showed them to be approximately spherical and uniform in size. Measurement of a statistical distribution of particles were made on the microscope micrometer scale, 0.7 microns per division. The distribution of sizes is shown in table 3. Statistical analysis of those particles sizes gave an average diameter of 1.6 microns.

Table 3. Frequency of Particles of Various Size in Sample of  $\text{Cs}_2\text{ReOCl}_5$

| Interval containing particle diameter, in scale divisions | Frequency |
|---|-----------|
| 3.5-3.7   | 1         |
| 3.2-3.4   | 2         |
| 2.9-3.1   | 2         |
| 2.6-2.8   | 10        |
| 2.3-2.5   | 10        |
| 2.0-2.2   | 32        |
| 1.7-1.9   | 26        |
| 1.4-1.6   | 7         |
| 1.1-1.3   | 7         |
| 0.8-1.0   | 3         |

The surface presented by each average sample size used in the exchange study was calculated from the formula:

$$S_{sp} = \frac{6}{D_s} d \quad \text{(IV)}$$

where  $S_{sp}$  = specific surface in  $\text{meter}^2/\text{gram}$

$D_s$  = average diameter with respect to surface,

d = density.

Using this equation the surface of the average sample of  $Cs_2-ReOCl_5$  used in the exchange study was  $0.82 \text{ m}^2/\text{gram} \times 2.2 \times 10^{-3} \text{ grams/sample} = 1.8 \times 10^{-3} \text{ m}^2$ .

### CHLORINE-36 EXCHANGE EXPERIMENT AND RESULTS

#### *Exchange Experiment for $K_2ReCl_6$*

Samples of  $K_2ReCl_6$  were weighed out in a 50 ml. beaker and dissolved in 1 ml of HCl. One hundred  $\lambda$  of Chlorine-36, having a specific activity of 26,237 counts per minutes per 100  $\lambda$ , was added. After standing for the appropriate time excess nitron acetate solution was added to precipitate nitron hexachlororhenate. The precipitate was filtered, washed twice with ml. portions of HCl, ethanol and ether. After drying under an infrared lamp the activity in the samples was measured in a Nuclear-Chicago Model D-47 gas flow counter.

Table 4 gives the details of the sample weights and counting times, and the results of the counting of activity in the samples.

Table 4. Exchange Data for  $K_2ReCl_6-Cl^{36}$  System

| Sample weights<br>(mg)<br>average of 3 | Exchange<br>Time | Average activity<br>in 3<br>Precipitates (c/m) | Activity in<br>Solutions<br>$\times 10^3$ (c/m) |
|--|------------------|--|---|
| 4.7                                    | 30 minutes       | 92   | 24.9  |
| 4.8                                    | 60               | 94   | 25.2  |
| 3.7                                    | 120              | 91   | 24.3  |
| 3.7                                    | 6 hours          | 78   | 23.8  |
| 4.2                                    | 24               | 91   | 24.1  |
| 4.4                                    | 48               | 98   | 23.8  |
| 4.3                                    | 2 weeks          | 88   | 24.2  |
| 3.7 ( $K_2ReO_4$ )                     | 30 minutes       | 77   | 24.8  |

An average of only 90 counts/minute of the 25,000 counts/minute from the solution were found in the 4 milligram samples. This amount of activity in each sample remained fairly constant over widely varying exchange times of from 30 minutes to six weeks, suggesting no progression of exchange, if any. Percent exchange was calculated as follows:

$$\text{percent exchange} = 100 \frac{(M_s)}{(M_c)} \frac{(A_i)}{(A_t)} \quad (V)$$

where  $M_s$  = millimoles of free  $Cl^-$

$M_c$  = millimoles of  $Cl^-$  in complex

$A_t$  = amount of activity remaining in the free  $Cl^-$  after the exchange

$A_1$  = amount of activity in complex after the exchange

In no case was there more than one 18% exchange indicated by the calculation. Enough time was allowed for a much higher percentage of exchange if an exchange reaction indeed were occurring.

The last sample (table 4) was  $K_2ReO_4$  treated in exactly the same manner as the  $K_2ReCl_6$  samples. Since it is known that oxygen atoms in  $K_2ReO_4$  will not be substituted by chlorines if placed in HCl solution, it is concluded that the 77 c/m, as well as the comparable activity in the hexachlororhenate precipitate was due to contamination and did not represent a significant exchange reaction. These results suggest that there is no appreciable exchange of chlorine atoms when  $K_2ReCl_6$  is dissolved in HCl<sup>36</sup> in agreement with conclusions of Jezowska, Trzbiatowska et al (3).

*Exchange Experiment for  $Cs_2ReOCl_5$*

The Chlorine-36 tracer used in the exchange experiment was in the form of KCl and was shown by analysis to have a concentration of  $1.54 \times 10^{-3}$  moles per liter of chlorine and a specific activity of 2024 + 24 counts per minute per 10  $\lambda$ .

Samples of  $Cs_2ReOCl_5$  were weighed by differences in a five cm. test tube. Two ml. of methanol were added as the exchange medium, and 10  $\lambda$  of Cl<sup>36</sup> was added. In order to ensure that all parts of the surface came in contact with the tracer, stirring was frequent throughout the exchange time. Several trials were run with samples of equal size. Temperature was kept constant during the exchange time. The samples were recovered by filtration, washed several times with methanol and dried with ether. After further drying under a heat lamp, the samples were counted in the gas-flow counter for ten minutes. The data obtained is shown in table 5.

Table 5. Exchange Data for the  $Cs_2ReOCl_5$ -Cl<sup>36</sup> System

| Trial | Sample Weight | Exchange Time | Activity in Recovered Sample, Corrected for Background |
|-------|---------------|---------------|--|
| 1     | 3.4 mg        | 30 minutes    | 15 cpm   |
| 2     | 3.5           | 45            | 18   |
| 3     | 3.4           | 90            | 17   |
| 4     | 3.4           | 30            | 15   |
| 5     | 3.4           | 30            | 19   |
| 6     | 3.3           | 60            | 11   |
| 7     | 3.4           | 60            | 15   |

The average activity in counts per minute above background for all samples recovered was 16. For exchange times as long as 90 minutes, no significant increase in count rate resulted. The average total count for sample plus background was 425 counts per ten minutes. The statistical deviation in the count rate was 21 counts per ten minutes or 2 counts per minute. Thus the average deviation in activity of samples was a statistical one.

Equation V was again used to calculate the percent exchange. In this case, however,  $M_c$  was defined as the number of millimoles in the complex on the total surface of the suspended  $Cs_2ReOCl_5$  sample. Having estimated the surface of the average sample and knowing the parameters of the unit cell  $M_c$  as defined was evaluated. The unit cell surface area was  $63.1 \times 10^{-20} M^2$ . Since the average sized sample surface was  $1.8 \times 10^{-3} M^2$ , the number of unit cell surfaces per surface of the average sample was  $2.9 \times 10^{15}$ . If only one hexagonal unit cell were involved, and completely immersed in the tracer, its two complex ions would be susceptible to exchange. However, if only one surface of the unit cell were exposed to the tracer, only an average of 1/3 of the complex ions would be susceptible to surface exchange. Therefore, there was  $2.9 \times 10^{15}$  unit cell surfaces  $\times$  1/3 or  $9.5 \times 10^{14}$  complex ions per surface of the average cell sample. No evidence was gathered, theoretical or experimental, to establish the orientation of the chlorine atoms with respect to the surface. Therefore, the most probable cases of orientation of 1, 2, or 3 chlorine atoms per unit cell on the sample surface were considered. This gave millimole values of  $1.6 \times 10^{-9}$ ,  $3.2 \times 10^{-9}$  for  $M_c$  to be used in equation V.

On the assumption that one chlorine atom per complex ion is at the surface per unit cell, these results estimate an exchange of 83%. On the assumption of 2 chlorine atoms per surface of the unit cell a 41% exchange is shown. Even on the less likely assumption of 3 chlorine atoms per surface of the unit cell a 28% exchange is shown. The fact that the percent of exchange did not increase with time (Table 5) further suggests that a rapid equilibrium distribution takes place between chlorine atoms in solution and on the surface of the  $ReOCl_5^-$ .

#### SUMMARY AND CONCLUSIONS

Chlorine atoms in  $K_2ReCl_6$  undergo only slight, if any, isotopic exchange when dissolved in HCl tagged with chlorine-36 in agreement with observations of Jezowska-Trzebidtowska et al (3). The surface chlorine atoms of insoluble  $Cs_2ReOCl_5$  undergo rapid isotopic exchange when suspended in methanol containing HCl tagged with Chlorine-36. These results are predicted by Taube's generalization (2) in that rhenium IV in octohedral complexes



with no vacant d orbitals are inert whereas rhenium V in octohe-  
dral complexes with one vacant d orbital is labile.

$\text{Cs}_2\text{ReOCl}_5$  is a yellow-brown compound, insoluble in dilute  
HCl. It crystallizes in a hexagonal system with unit cell parameter  
of  $a = 7.04\text{\AA}$  and  $c = 10.9\text{\AA}$ .

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