

## The Structure of a Cubic Hydrogen Rhenium Bronze, $H_{1.36}ReO_3$

P. G. DICKENS\* AND M. T. WELLER

*Inorganic Chemistry Laboratory, Oxford, England*

Received December 8, 1982; in revised form March 21, 1983

The structure of  $D_{1.36}ReO_3$  has been determined by a room temperature powder neutron diffraction study. The unit cell is body centered cubic (space group  $Im\bar{3}$ ) and contains eight formula weights ( $a = 7.497 \pm 0.001 \text{ \AA}$ ). A least squares method based on peak intensities was used to refine the structure. The rhenium atoms lie on the special perovskite sites and are surrounded by distorted octahedra of oxygen atoms which are displaced towards the vacant perovskite *A* sites. The deuterium atoms are statistically distributed over 72 possible sites in the unit cell, as OD bonds.

### Introduction

Hydrogen insertion compounds of transition metal oxides of general formula  $H_xMO_n$  with  $0 \leq x \leq 2$  are well known (1). Examples are the hydrogen tungsten and molybdenum bronzes,  $H_xWO_3$ ,  $0 \leq x \leq 0.6$  (2) and  $H_xMoO_3$ ,  $0 \leq x \leq 2.0$  (3). Hydrogen insertion into these oxides leaves the parent oxide lattice substantially unchanged.

The preparation of a hydrogen rhenium bronze,  $H_{0.15}ReO_3$ , was originally reported by Kimizuka *et al.* (4). An orthorhombic phase of higher hydrogen content was later described by these workers (5). Following these reports we have prepared a series of hydrogen rhenium bronzes  $H_xReO_3$  with  $0 \leq x \leq 1.36$ . Powder X-ray photographs of  $H_{1.36}ReO_3$  showed strong lines characteristic of a simple cubic lattice but also revealed some very weak lines which could be indexed on a cubic unit cell having approximately double the lattice constant of  $ReO_3$  (Table I).

A similar superlattice has also been

found for cubic  $H_{0.53}WO_3$  and results from a distortion of the  $WO_3$  framework (6). In the present work a powder neutron diffraction study has been undertaken to determine the crystal structure of  $D_{1.36}ReO_3$ .

### Sample Preparation and Analysis

#### $ReO_3$

Crystalline  $ReO_3$  was prepared from high purity  $NH_4ReO_4$ . The perrhenate was reduced under flowing hydrogen at  $450^\circ C$  and the rhenium metal so produced was oxidized to  $Re_2O_7$  in a static oxygen environment (7). The  $Re_2O_7$  was purified by sublimation and then reduced to  $ReO_3$  according to the prescription of Nechamkin (8) using dioxane.

#### $D_xReO_3$

Insertion of deuterium into  $ReO_3$ , to give  $D_xReO_3$ , was carried out using gaseous deuterium in the presence of a Pt catalyst (9).  $ReO_3$  was treated with an aqueous solution of  $H_2PtCl_6$  and the solvent removed under vacuum to yield a  $ReO_3/H_2PtCl_6$  ratio of

\* To whom correspondence should be addressed.

TABLE I  
POWDER X-RAY DATA FOR  $D_{1.36}\text{ReO}_3$

Intensity	$d_{\text{calc}}$	$d_{\text{obs}}$	$h$	$k$	$l$
S	3.747	3.749	2	0	0
S	2.651	2.648	2	2	0
VVW	2.371	2.367	3	1	0
S	2.162	2.162	2	2	2
VVW	2.003	2.002	3	2	1
S	1.874	1.873	4	0	0
MS	1.676	1.676	4	2	0
MS	1.530	1.529	4	2	2
MS	1.325	1.326	4	4	0
MS	1.249	1.250	4	4	2
M	1.185	1.185	6	2	0

Note: Refined parameters  $7.497 = a = b = c$ .

25:1. The sample, at 298 K, was then exposed to deuterium gas and the insertion reaction which occurred over a period of 24 hr was followed by volumetric gas absorption. The chloroplatinic acid is reduced *in situ* to yield finely dispersed platinum that catalyzes the reaction. A Guinier X-ray photograph of the product showed a pure cubic phase of lattice content (subcell)  $a = 3.749 \pm 0.001 \text{ \AA}$ .

The rhenium oxidation state in the product was measured potentiometrically using 0.05 M ceric sulphate solution. The gaseous uptake of deuterium by  $\text{ReO}_3$  and the metal oxidation state in the product were consistent with the formula  $D_{1.36}\text{ReO}_3$ .

### Neutron Diffraction

Neutron diffraction measurements were performed at room temperature on a powder diffractometer, 10 HPD, at the reactor DIDO, AERE Harwell. The sample was loaded into a 12-mm diameter vanadium can sealed with a rubber O-ring to avoid decomposition of the air sensitive compound. The angular range of  $2\theta$  from 10 to  $90^\circ$  was scanned and a neutron wavelength of  $0.996 \text{ \AA}$  used.

The observed reflections were indexed

on a cubic unit cell with lattice constant  $2a$  and the systematic absence  $h + k + l = 2n + 1$  found. The intensity of the superlattice reflections could be accounted for by oxygen displacements represented by the special position  $24(g)$  of the space group  $Im\bar{3}$ . At low angles the peak spacing allowed the intensity of each peak to be determined accurately and hence a profile refinement was superfluous (10) and the integrated intensity analysis was used.

The refinement of atomic positions was carried out using a computer program written by Wiseman (11). This program minimizes the function

$$\sum_i \omega_i (I_{\text{obs}_i} - I_{\text{calc}_i})^2.$$

Twenty high intensity peaks were chosen for the refinement, each weighted according to the standard deviation of the intensity as estimated from counting statistics. The neutron scattering lengths used were  $b_D = 0.667 \times 10^{-12} \text{ cm}$ ,  $b_{\text{Re}} = 0.92 \times 10^{-12} \text{ cm}$ , and  $b_O = 0.580 \times 10^{-12} \text{ cm}$  (12).

### Structure Refinement

The early stages of the refinement were carried out with the deuterium atoms omitted from the structure. The rhenium and oxygen atoms were initially placed on the  $\text{ReO}_3$  special sites; an  $R_1$  index  $[100\sum(I_{\text{obs}} - I_{\text{calc}})]/\sum_{\text{obs}}$  of 60% resulted. Refinement of the oxygen positions lead to a shift along 011 as given by the positions  $24(g)$  (0, y, z) of  $Im\bar{3}$  and  $R_1$  fell to a value of 12.1%. A Fourier difference synthesis located the deuterium atoms which were then assigned an isotropic temperature factor of  $5.0 \text{ \AA}^2$  (Fig. 1). The total occupation for deuterium was constrained to yield 10.88 atoms per unit cell corresponding to the formula  $D_{1.36}\text{ReO}_3$ , and the temperature factors for different deuterium atoms were constrained to be equal. Refinement of atomic coordinates and temperature factors for oxygen

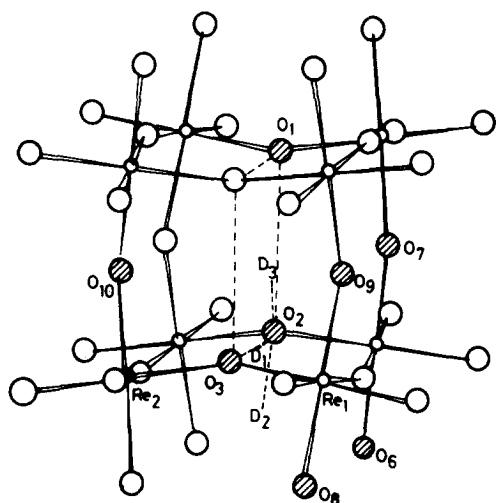


FIG. 1. The eight ReO<sub>6</sub> octahedra surrounding (0,0, $\frac{1}{2}$ ) in D<sub>1.36</sub>ReO<sub>3</sub>.

and deuterium, and the rhenium temperature factor lead to convergence and a final  $R_I$  factor of 2.04%.

The agreement between observed and calculated peak intensities is given in Table II, and the final positional and thermal parameters together with their estimated standard deviations are given in Table III. A final difference Fourier map was synthesized and showed no extra peaks consistent with possible site occupancy.

### Discussion

Table IV shows a number of important bond lengths and angles deduced for cubic

TABLE II  
OBSERVED AND CALCULATED INTENSITIES FOR  
H<sub>1.36</sub>ReO<sub>3</sub>

$h$	$k$	$l$	$I_{\text{calc}}$	$I_{\text{obs}}$	$\sigma(I_{\text{obs}})$
2	0	0	42.2	42.3	0.26
3	1	0	8.99	9.05	0.45
2	2	2	1.29	1.31	0.82
3	2	1	6.68	6.60	0.56
4	0	0	32.6	32.6	0.46
4	2	0	38.1	38.1	0.42
4	2	2	10.9	10.8	0.55
5	1	0	3.87	3.50	0.80
1	3	4			
4	4	0	17.8	17.8	0.35
5	3	0	3.82	4.17	0.57
4	4	2	17.2	17.0	0.34
5	3	2	3.48	3.22	0.73
6	2	0	3.64	4.14	0.65
4	4	4	5.38	5.61	0.62
6	4	0	6.63	6.54	0.60
6	4	2	10.7	10.8	0.57
8	2	0			
6	4	4	16.9	16.3	0.60
8	2	2			
6	6	0	6.14	6.78	0.75
8	4	2	15.3	16.3	0.60
10	2	0			
8	6	2	13.7	13.1	0.65

D<sub>1.36</sub>ReO<sub>3</sub>. The values refer to the contents of the average unit cell of the crystal.

The rhenium atoms form a primitive cubic lattice and each metal atom has a distorted octahedral arrangement of oxygen atoms around it. The distortion of the oxygen sublattice results in the formation of

TABLE III  
ATOMIC PARAMETERS FOR D<sub>1.36</sub>ReO<sub>3</sub>

Atom	Position	$x$	$y$	$z$	$B(\text{\AA}^2)$	Atoms/Unit cell
Re	8(c)	0.25	0.25	0.25	0.13(2)	8.0
O	24(g)	0.0	0.242(1) <sup>a</sup>	0.294(1)	1.83(16)	24.0
D <sub>1</sub>	24(g)	0.0	0.114(14)	0.281(12)	5.6(1.0)	4.82(0.5)
D <sub>3</sub>	24(g)	0.0	0.207(13)	0.435(13)	5.6(1.0)	2.56(0.7)
D <sub>2</sub>	24(g)	0.0	0.179(12)	0.169(14)	5.6(1.0)	3.50(0.5)

<sup>a</sup> Estimated standard deviations in parentheses.

TABLE IV

Bond distances (Å)		Bond angles (°)	
Re <sub>1</sub> -Re <sub>2</sub>	3.749	O <sub>7</sub> -Re-O <sub>7</sub>	98.3
Re <sub>1</sub> -O <sub>3</sub>	1.904	O <sub>7</sub> -Re-O <sub>6</sub>	81.7
O <sub>1</sub> -O <sub>2</sub>	3.09	Re <sub>1</sub> -O <sub>3</sub> -Re <sub>2</sub>	169.1
O <sub>2</sub> -O <sub>3</sub>	3.63	D <sub>1</sub> -O <sub>7</sub> -O <sub>3</sub>	5.8
O <sub>7</sub> -O <sub>9</sub>	3.87	D <sub>3</sub> -O <sub>7</sub> -O <sub>1</sub>	13.9
O <sub>9</sub> -O <sub>10</sub>	4.41	D <sub>7</sub> -O <sub>7</sub> -O <sub>3</sub>	63.3
O <sub>2</sub> -D <sub>1</sub>	0.96		
O <sub>2</sub> -D <sub>2</sub>	1.05		
O <sub>2</sub> -D <sub>3</sub>	1.09		

nonequivalent A sites from the original perovskite structure. Of the eight original equivalent sites, six sites occur for which the local environment is provided by four oxygen sites which have been displaced towards the interstitial site.

The deuterium atoms are randomly attached to all the oxygen atoms as deuterioxy bonds which are about 1 Å long. The O-D . . . O distance is too large in all cases for hydrogen bonding to occur. The deuterium atoms are distributed over a possible 72 positions in the unit cells; however, some arrangements of deuterium atoms among these sites cannot occur since this would give rise to impossibly short interatomic distances.

The structure was supported by NMR evidence. The second moment for a sample of H<sub>1.36</sub>ReO<sub>3</sub> was measured at 150 K to be  $3.7 \pm 0.5$  G<sup>2</sup>. Such a small value excludes the possibility of OH<sub>2</sub> groupings in the structure, and agrees with a value computed for a random distribution of hydrogen over the possible sites determined by neutron diffraction (after the exclusion of simultaneous occupancy for chemically unreasonable distances.)

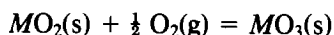
Insertion of deuterium into ReO<sub>3</sub> causes the Re-O bond length to increase, from 1.87 Å in ReO<sub>3</sub> to 1.90 Å in D<sub>1.36</sub>ReO<sub>3</sub>, but the tilting of the octahedra that occurs causes the cell volume to remain almost constant.

The structure of cubic D<sub>1.36</sub>ReO<sub>3</sub> was found to be very similar to that of D<sub>0.53</sub>WO<sub>3</sub> (6). However, the larger deuterium content of the rhenium compound results in a larger number of sites being occupied by deuterium and a greater distortion of the MO<sub>6</sub> groups away from perfect octahedra is also observed.

The crystal structure shows that the hydrogen rhenium bronze should be classified as a nonstoichiometric oxide hydroxide ReO<sub>3-x</sub>(OH)<sub>x</sub>. In the limiting case  $x = 3$  a hydroxide M(OH)<sub>3</sub> would result and this structure is also found for the trivalent hydroxides Sc(OH)<sub>3</sub>, In(OH)<sub>3</sub>, and Lu(OH)<sub>3</sub>. The distortions in these hydroxides from the perfect oxygen sublattice of ReO<sub>3</sub> are much larger and hydrogen bonding occurs. The difference may be due in part to there being insufficient hydrogen atoms in H<sub>x</sub>ReO<sub>3</sub> to bind all the oxygen atoms together, whereas in In(OH)<sub>3</sub> there is one hydrogen atom between every pair of oxygen atoms.

The random distribution of deuterium among the sites is in good agreement with the potential distribution in the lattice. Calculations of Horiuchi *et al.* (5) show a potential valley  $\sim 1.00$  Å from oxygen containing shallow potential minima. The hydrogen atoms are therefore likely to be randomly distributed over sites  $\sim 1.00$  Å from oxygen with higher probability of occupation of sites of the least potential. The shallowness of the potential minima is reflected in the fairly high temperature factors determined for deuterium.

The values of maximum hydrogen content for the bronzes H<sub>x</sub>MO<sub>3</sub>, prepared by hydrogen spillover ( $M = W, Re, \text{ and } Mo, x = 0.36, 1.36, \text{ and } 1.68$ , respectively), parallel the values of  $-\Delta G^0$  (298 K) for the reaction



$$-\Delta G^0 (298K) = 230 \text{ kJ mol}^{-1} (W),$$

$$153 \text{ kJ mol}^{-1} (Re), \text{ and } 135 \text{ kJ mol}^{-1} (Mo).$$

This suggests that the limiting  $x$  value obtained (at  $p\text{H}_2 = 1$  atm, 298 K) is of thermodynamic rather than crystallographic origin and is associated with the ease of reduction of the VI oxidation state of the metal concerned.

### Acknowledgments

The authors thank the AFOSR for financial support (Grant 83-0052), and the Kent LEA for a research grant for one of us (MTW).

### References

1. R. SCHOLLHORN, *Ange. Chemie* **19**, 983, Inter. Ed. in England.
2. P. G. DICKENS AND R. J. HURDITCH, *Nature* (London) **215**, 289 (1971).
3. J. J. BIRTILL AND P. G. DICKENS, *Mater. Res. Bull.* **13**, 311 (1978).
4. N. KIMIZUKA, T. AKAHANE, S. MATSUMOTO, AND K. YUKINO, *Inorg. Chem.* **15**, 3178 (1976).
5. S. HORIUCHI, N. KIMIZUKA, AND A. YAMAMOTO, *Nature* (London) **279**, 226 (1979).
6. P. J. WISEMAN AND P. G. DICKENS, *J. Solid State Chem.* **6**, 374 (1973).
7. A. D. MELAVEN, J. N. FOWLE, W. BRICKELL, AND C. F. HISKEY, *Inorg. Synth.* **3**, 188 (1950).
8. M. NECHAMKIN, A. N. KURTZ, AND C. F. HISKEY, *J. Amer. Chem. Soc.* **73**, 2828 (1951).
9. G. C. BOND AND P. A. SERMON, *Catal. Res.* **8**, 211 (1973).
10. M. SAKATA AND M. J. COOPER, *J. Appl. Crystallogr.* **12**, 554 (1979).
11. P. J. WISEMAN, Ph.D. thesis, I.C.L. Oxford.
12. G. BACON, *Acta Crystallogr. Sect. A* **28**, 357 (1972).