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X-Ray Determination of the Crystal Structure of Potassium Rhenium Hydride

BY K. KNOX AND A. P. GINSBERG

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The crystal structure of K_2ReH_9 has been determined by single crystal X-ray diffraction. The substance is hexagonal, $a = 9.607 \pm 0.005$ and $c = 5.508 \pm 0.005$ Å., with three formula weights in the unit cell. The most probable space group is D^3_{3h}-P$\bar{6}$2m in which one Re occupies position 1(a), (000), and two Re 2(d), $\pm(^1/_3{}^2/_3{}^1/_2)$, while there are three K in 3(f), (x00, etc.), with $x = 0.5900 \pm 0.0016$, and three K in 3(g), ($x0^1/_2$, etc.), with $x = 0.2573 \pm 0.0012$. The closest approach of Re atoms to one another in this compound is 5.51 Å., so that the Re atoms exist as discrete ReH_9^{-2} units. Although the two rhenium atoms are crystallographically different, their environments are essentially the same, each being surrounded by nine potassium ions arranged in a trigonal prism with three atoms directly beyond or nearly directly beyond the centers of the prism faces. This arrangement, along with the Re–K distances which average 3.83 Å., leaves ample space for nine hydrogen atoms around the Re.

Introduction

The X-ray structure determination of the unusual transition metal hydride K_2ReH_9[1-3] is of interest for several reasons. First of all, it provides an independent confirmation of the K:Re ratio in the compound. This is important because of the existing controversy concerning the composition.[1,3,4] Secondly, the results, coupled with the known chemical behavior of the hydride, demonstrate the existence of discrete ReH_9^{-2} anions. Finally, the X-ray work is a necessary preliminary to the interesting problem of the location of the hydrogens and the structure of the ReH_9^{-2} ion which has been carried out by neutron diffraction in collaboration with Abrahams.[3]

Experimental

Single crystals of anhydrous K_2ReH_9 were grown by slow evaporation of an aqueous KOH solution of the compound. The crystals are hexagonal with $a = 9.607 \pm 0.005$ and $c = 5.508 \pm 0.005$ Å.; the unit cell contains three formula weights, and d_m is 3.07 g. cm.$^{-3}$, d_x 3.094 g. cm.$^{-3}$. The high absorption coefficient for Mo Kα X-rays, $\mu = 245$ cm.$^{-1}$, necessitated correction for absorption. To facilitate this a sphere 0.15 mm. in radius was ground in a Bond sphere grinder[5] and mounted in a sealed Lindemann glass capillary. Diffraction data were collected using Mo Kα radiation and controlled exposure times with the precession camera for the $h0l$ layer and with Abrahams'[6] version of the Weissenberg camera for the $hk0$ layer. Intensities were estimated visually by comparison with a calibrated strip made from the crystal. The usual Lorentz and polarization corrections were applied along with absorption corrections calculated using a program written by J. Sautter, formerly of Bell Laboratories.

Determination of the Structure

The diffraction symmetry of D_{6h} with no systematic absences, observed both on the two zero-level photographs taken for intensity measurements and on upper level survey photographs, indicates space groups D^1_{6h}-P6/mmm, D^1_{3h}-P$\bar{6}$m2, D^3_{3h}-P$\bar{6}$2m, C^1_{6v}-P6mm, or D^1_6-P622 as the most probable. The main features of the diffraction can only be fitted by placing three Re in 000 and $\pm{}^1/_3{}^2/_3{}^1/_2$. Patterson projections on (001) and (010), besides verifying the Re positions, indicated clearly Re–K vectors along x,0,0, etc., not x,2x,0, etc., with $x \cong {}^1/_4$. This short distance of 2.4 Å. between the c-axis and the potassium ions rules out the space groups with 6-fold axes, D^1_{6h}, C^1_{6v}, and D^1_6, for in them the six K^+ produced by this axis would be too close to each other. D^1_{3h} is also highly improbable because the 6(l) or 6(m) positions become essentially those of a 6-fold axis when $y \approx 0$. In the remaining space group, D^3_{3h}, the 6(j) and (6k) positions degenerate to 3(f) and 3(g) when $y \sim 0$. Furthermore, the (010) Patterson projection shows a Re–K vector of $(0,{}^1/_2)$ so that the 6(i) position with $z = {}^1/_2$ degenerates to 3(g). The most reasonable trial structure then, on the basis of the structure factors and on stereochemical grounds, was obtained with the atoms in the following positions of D^3_{3h}-P$\bar{6}$2m

1 Re_1 in 1(a): (000)
2 Re_2 in 2(d): $\pm(^1/_3{}^2/_3{}^1/_2)$
3 K_1 in 3(f): $(x00, 0x0, \bar{x}\bar{x}0)$ with $x \approx {}^1/_2$
3 K_2 in 3(g): $(x0^1/_2, 0x^1/_2, \bar{x}\bar{x}^1/_2)$ with $x \approx {}^1/_4$

This trial structure was verified by the subsequent refinement, even though a test for piezoelectricity by the method of Giebe and Scheibe proved negative, and the statistical tests[7] for a center of symmetry on the $hk0$

TABLE I

REFINED ATOMIC COORDINATES AND TEMPERATURE FACTORS OF K_2ReH_9

	x	B
K_1	0.5900 ± 0.0016	3.27 ± 0.23
K_2	0.2573 ± 0.0012	2.42 ± 0.16
Re_1		1.77 ± 0.07
Re_2		2.06 ± 0.07

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(1) A. P. Ginsberg, J. M. Miller, and E. Koubek, *J. Am. Chem. Soc.*, **83**, 4909 (1961).

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(3) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *ibid.*, **3**, 558 (1964). It is shown in this paper that the hydride contains nine hydrogens per Re rather than eight as reported in ref. 1.

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TABLE II

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

*hk*0

h	$\|F_o\|$	$\|F_c\|$	α°	*h*	$\|F_o\|$	$\|F_c\|$	α°	*h*	$\|F_o\|$	$\|F_c\|$	α°	*h*	$\|F_o\|$	$\|F_c\|$	α°	*h*	$\|F_o\|$	$\|F_c\|$	α°	*h*	$\|F_o\|$	$\|F_c\|$	α°
	*h*00				*h*10				*h*20 (*contd.*)				*h*30 (*contd.*)				*h*40 (*contd.*)				*h*60		
1	[b]	3.9	0	1	165.3	178.2	0.7	3	20.5	19.2	283.3	5	11.3	11.6	341.5	7	79.4	68.2	3.2	6	55.8	50.6	354.6
2	[b]	13.3	0	2	44.8	48.5	109.7	4	25.3	23.6	131.6	6	80.8	81.7	346.9	8	−6.3	9.5	352.5	7	−6.4	3.0	235.5
3	183.1	224.4	0	3	31.2	28.3	266.1	5	123.3	127.5	5.2	7	−6.0	7.1	317.9	9	−6.4	4.1	88.9	8	−6.5	1.5	237.6
4	31.1	30.5	0	4	136.5	158.0	2.6	6	8.0	8.0	152.5	8	−6.2	5.9	319.0	10	38.9	33.5	359.5	9	31.9	28.6	6.2
5	28.7	29.7	0	5	22.3	19.5	132.9	7	−5.9	6.1	269.3	9	65.4	53.0	357.4	11	−6.5	3.8	19.0	10	−6.5	2.1	268.0
6	96.3	113.1	0	6	13.5	9.1	166.0	8	88.9	70.7	3.2	10	−6.4	5.2	270.7	12	−6.5	3.6	7.2	11	−6.5	1.6	278.0
7	25.2	22.8	0	7	92.1	101.1	2.0	9	−6.2	8.9	105.9	11	−6.5	3.7	282.4	13	12.9	16.3	0.4	12	12.8	13.8	3.3
8	23.4	17.6	0	8	−5.9	6.2	265.4	10	−6.3	4.0	318.7	12	38.1	28.2	1.1		*h*50				*h*70		
9	88.5	75.0	0	9	−6.1	10.7	107.9	11	44.6	34.6	358.2	13	−6.5	2.1	308.1	5	75.5	82.3	6.6	7	41.8	38.8	335.5
10	−6.2	5.5	0	10	61.3	50.5	1.8	12	−6.5	2.3	47.1	14	−6.4	1.6	300.9	6	−6.1	4.6	126.7	8	−6.5	5.4	7.5
11	−6.3	5.1	0	11	−6.4	4.0	327.9	13	−6.5	2.2	62.1	15	12.4	11.5	356.9	7	−6.3	9.6	351.2	9	−6.5	2.0	0.4
12	59.7	46.8	0	12	−6.5	2.7	45.1	14	15.9	16.9	358.5		*h*40			8	50.9	45.5	0.6	10	22.5	19.4	354.9
13	−6.5	1.7	0	13	32.0	24.3	2.9		*h*30			4	110.1	117.8	6.2	9	−6.5	3.8	88.3		*h*80		
14	−6.5	1.6	0		*h*20			3	130.1	133.9	348.0	5	−5.8	3.6	348.4	10	−6.5	3.4	28.7	8	30.7	26.8	357.1
15	31.8	20.9	0	2	158.6	171.3	2.6	4	18.7	13.6	338.7	6	−6.0	6.2	128.5	11	27.7	23.2	357.8		*h*90		
																				9	15.7	14.5	9.3

*h*0*l*

h	$\|F_o\|$	F_c	*h*	$\|F_o\|$	F_c	*h*	$\|F_o\|$	F_c	*h*	$\|F_o\|$	F_c	*h*	$\|F_o\|$	F_c	*h*	$\|F_o\|$	F_c	*h*	$\|F_o\|$	F_c	*h*	$\|F_o\|$	F_c
	*h*00			*h*01			*h*02			*h*03			*h*04			*h*05			*h*06			*h*07	
1	[b]	3.9	0	[b]	−72.9	0	311.8	269.1	0	47.4	−52.6	0	183.1	164.7	0	32.1	−32.0	0	96.3	92.1	0	16.1	−17.2
2	[b]	13.3	1	139.8	117.6	1	−4.3	3.8	1	94.9	88.6	1	−5.1	3.7	1	60.7	56.8	1	−4.8	3.5	1	28.7	32.2
3	224.1	224.4	2	193.4	175.5	2	8.7	10.1	2	145.3	122.9	2	−5.1	5.9	2	75.2	74.1	2	−4.7	3.6	2	37.9	40.4
4	31.3	30.5	3	60.1	−60.9	3	216.4	188.3	3	45.8	−44.9	3	139.6	125.2	3	28.1	−27.4	3	74.4	73.2	3	12.6	−14.4
5	30.0	29.7	4	73.7	75.5	4	24.6	25.1	4	65.1	61.2	4	14.2	16.7	4	43.7	41.2	4	10.0	10.5	4	22.1	24.1
6	100.6	113.1	5	110.4	112.8	5	23.4	21.7	5	92.6	86.5	5	15.7	16.0	5	54.1	55.4	5	9.5	9.3	5	mw[c]	31.0
7	24.0	22.8	6	38.4	−37.8	6	103.5	101.0	6	31.3	−29.0	6	78.3	73.8	6	18.5	−18.0	6	48.8	46.1			
8	17.2	17.6	7	68.2	71.7	7	19.8	20.0	7	53.9	57.5	7	13.5	14.2	7	38.9	38.6	7	8.4	8.8			
9	71.0	75.0	8	44.4	47.9	8	14.0	15.8	8	37.4	39.4	8	11.1	11.9	8	26.4	27.3						
10	−4.7	5.5	9	19.6	−21.1	9	60.8	68.0	9	18.3	−16.9	9	51.2	51.1									
11	−4.0	5.1	10	41.5	47.6	10	−4.4	5.0	10	38.9	39.3	10	vw[c]	3.9									
			11	22.0	26.3	11	−3.3	4.8															

[a] − preceding $|F_o|$ indicates unobserved reflections for which tabulated value is one-half of local estimated minimum observable. [b] On intense white streak; no accurate estimate possible. [c] On edge of sphere of reflection; no accurate Lorentz-polarization correction possible.

data gave nonsensical results, as was anticipated, because this crystal does not meet the conditions of the tests.

The refinement of the structure was done using the full-matrix least-squares program of Busing and Levy.[8] Initially unit weights were assigned to all observed and zero weights to the unobserved reflections. The scattering factors used were that for K^+ of Berghuis, *et al.*,[9] and that for Re of Thomas and Umeda.[10] The calculation converged rapidly with eight parameters: two scale factors, two x parameters for the potassium ions, and four isotropic temperature factors. Then the weights were adjusted using Cruickshank's scheme.[11] The unobserved reflections in both layers were assigned $|F|$ values equal to one-half of the local estimated minimum observable value. The 100; 200; 10,0,4; and 507 reflections were given zero weights for reasons set out in Table II. Again the calculation converged rapidly with no significant changes in the parameters; the two scale factors and four temperature factors changed by one to two standard deviations while the two positional parameters altered by only one-fifth of their σ values. The weighted R value including the unobserved reflections became 0.115. The final values for the refined atomic parameters with their standard deviations are given in Table I and the observed and calculated structure factors in Table II.

In a crystal structure such as K_2ReH_9, where the heavy atoms dominate the scattering, it is possible to get good agreement between observed and calculated structure factors with only the heavy atoms correctly placed. The comparatively low standard deviations on the potassium ions, however, together with the fact that all of the unobserved reflections have a calculated value less than the minimum observable, show that the structure is essentially correct. Nevertheless, $hk0$ Fourier syntheses were now carried out to increase the certainty of the structure. The projection on (001) of the observed structure factors with the calculated phases showed reasonably circular atoms of about the correct size and with integrated electron densities corresponding to the correct numbers of electrons. It is shown in Fig. 1. The F_{calcd} projection in addition gave positional parameters for the K^+ less than one standard deviation away from the least-squares values, indicating that no shifts are necessary. Finally, the difference Fourier had uniform positive and negative regions with peaks and depressions one-fourth or less the size of the K^+ ion. The structure can then be taken to be correct, and this refinement, in conjunction with previous chemical[1] and physical[2] evidence, provides further confirmation for K:Re = 2 in the formula, not K:Re = 1. If one-half of the potassium ions had been omitted in the refinement, they would have appeared in the difference Fourier synthesis.

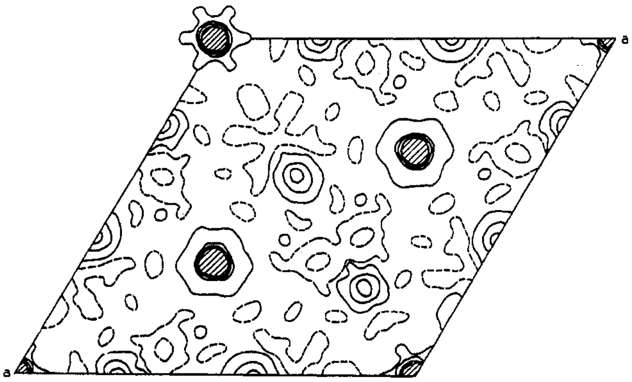

Fig. 1.—Final (001) Fourier projection. Contours are given at 0 (dashed), 10, 30, and 50 on an arbitrary scale.

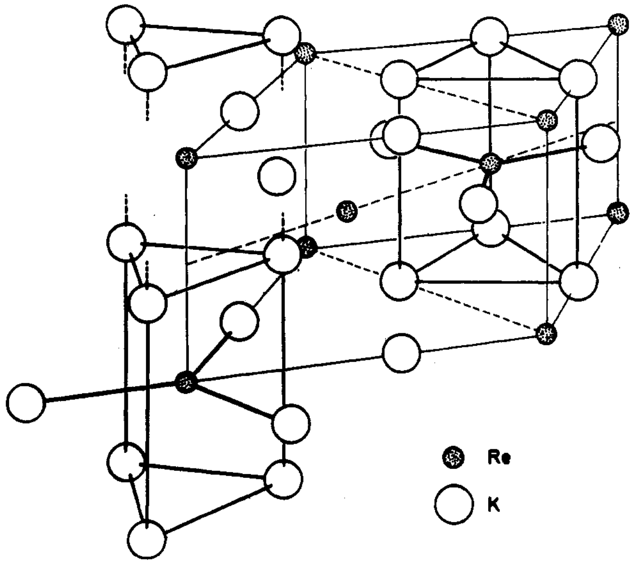

Fig. 2.—The arrangement of the metal atoms in the unit cell of K_2ReH_9.

Discussion of the Structure

The arrangement of the metal ions in K_2ReH_9 is shown in Fig. 2. A feature of interest is the large distances between rhenium atoms; 5.51 Å. from Re_1 to Re_1 along the c-axis and 5.55 Å. from Re_2 to Re_2, with the Re_1–Re_2 distance even larger. Thus, direct bonding between rhenium atoms is precluded, and so they exist in discrete ReH_9^{-2} units. Although the Re atoms are crystallographically nonequivalent, their environments of K^+ ions turn out to be essentially the same. Each Re is surrounded by nine K^+ arranged in a trigonal prism with three ions beyond the centers of the prism faces, a common geometry for coordination number nine. These arrangements are outlined in Fig. 2, and the interatomic distances are given in Table III.

TABLE III

Re–K DISTANCES IN K_2ReH_9

$Re_1(000)$	6 K at 3.701 ± 0.008 Å.
	3 K at 3.939 ± 0.015 Å.
$Re_2(^1/_3{}^2/_3{}^1/_2)$	6 K at 4.003 ± 0.007 Å.
	3 K at 3.623 ± 0.013 Å.

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For Re_2 with site symmetry C_{3h}-$\bar{6}$, the triangle of K^+ ions at the prism faces is not required to be rotated exactly 60° with respect to the triangles of the prism top and bottom, but, in fact, it is only slightly less than 4° from this position. Furthermore, the averages of the nine Re–K distances in the two different prisms, 3.78 and 3.88 Å., respectively, are nearly equal. Thus, the nonequivalence of the Re atoms appears to be a matter of crystallographic description rather than a fundamental physical or chemical difference, in agreement with previous studies.[1,2]

The potassium ions are far enough from the Re for there to be plenty of space around the Re to accommodate the hydrogen atoms, even though the latter may occupy an appreciable amount of space.

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Transition Metal–Hydrogen Compounds. II.
The Crystal and Molecular Structure of Potassium Rhenium Hydride, K_2ReH_9

By S. C. ABRAHAMS,[1] A. P. GINSBERG, and K. KNOX

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A neutron diffraction analysis of K_2ReH_9 has established the composition of this unusual potassium rhenium hydride. Further chemical analysis has verified the stoichiometry. The hydrogen atom positions have been determined within space group $P\bar{6}2m$ as: three H in (3f) ($x00$, etc.) with $x = 0.1789 \pm 0.0024$; six H in 6(i) ($x0z$, etc.) with $x = 0.8789 \pm 0.0014$, $z = 0.2171 \pm 0.0032$; six H in 6(k) ($xy^1/_2$, etc.) with $x = 0.1483 \pm 0.0018$, $y = 0.6250 \pm 0.0024$; and twelve H in 12(l) (xyz, etc.) with $x = 0.2240 \pm 0.0010$, $y = 0.5254 \pm 0.0013$, $z = 0.7125 \pm 0.0020$. The two crystallographically independent Re atoms are essentially equivalent. Both are at the centers of trigonal prisms of H atoms, with three additional H atoms beyond the centers of the prism faces. The average Re–H distance is 1.68 ± 0.01 Å.; the average H–Re–H angle between hydrogens in the same vertical mirror plane is 93.6 ± 0.6°. An elementary LCAO–MO description of the ReH_9^{-2} ion is given. The optical spectrum of K_2ReH_9 in alkaline aqueous solution is reported. The band observed at 46,080 cm.$^{-1}$ is assigned as a transition between bonding and antibonding molecular orbitals. The absorption intensity is related to the polarity of the MO's. It is concluded that the bonding MO's involving the Re 5d orbitals are most likely polarized toward the H atoms. The n.m.r. and exchange equivalence of all the hydrogens in ReH_9^{-2} is explained by their similar environment and by the existence of deformation modes which, with small displacements, can interchange the prism and equatorial hydrogens.

Introduction

The nature of the reactive rhenium compound obtained by reduction of perrhenate, in aqueous ethylenediamine solutions, with potassium metal has been the subject of some controversy. Bravo, Griswold, and Kleinberg,[2] the first to study the reaction, obtained a product which they believed to be $KRe \cdot 4H_2O$ in impure form. They identified this with Lundell and Knowles' rhenide,[3] prepared by reduction of acid perrhenate solutions with zinc amalgam and known only in dilute solution. In 1959 Floss and Grosse[4] claimed to have isolated the rhenide, $KRe \cdot 4H_2O$, in pure form. However, in 1960, Ginsberg, *et al.*,[5] reported chemical and nuclear magnetic resonance evidence showing the product described by Bravo, Griswold, and Kleinberg to be a potassium rhenium hydride with hydrogen directly bonded to the rhenium. Floss and Grosse thereupon revised their formula to $KReH_4 \cdot 2H_2O$.[6] This formula is in disagreement with the conclusions of Ginsberg, Miller, and Koubek,[7] who found the hydride to have the stoichiometry K_2ReH_8. That the two hydrides are the same is shown by their identical infrared spectra[7] and the similarity of their methods of preparation. The relation between the hydride formed by reduction of perrhenate with alkali metals and Lundell and Knowles' rhenide has also been discussed recently.[8] It was concluded, on the basis of spectroscopic and polarographic evidence, that these must be different species, although rhenide is also probably a rhenium hydride.

The formula K_2ReH_8 for the hydride gave rise to two objections, since the rhenium is formally in the +6 oxidation state with a $5d^1$ electron configuration. Such a material might be expected to show both color and temperature-dependent paramagnetism, neither of which is found.[7,9] In an effort to find an explanation for these facts, X-ray and neutron diffraction investigations of the structure of potassium rhenium hydride were initiated. The X-ray results have already been re-

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