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.

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

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) ($xy\frac{1}{2}$, 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 $93.6 \pm 0.6°$. 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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(2) J. Bravo, E. Griswold, and J. Kleinberg, *J. Phys. Chem.*, **58**, 18 (1954).
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(7) A. P. Ginsberg, J. M. Miller, and E. Koubek, *J. Am. Chem. Soc.*, **83**, 4909 (1961).
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(9) K. Knox and A. P. Ginsberg, *Inorg. Chem.*, **1**, 945 (1962).

ported.[9,10] The X-ray work, which was preliminary to the neutron diffraction study, located the potassium and rhenium atoms and confirmed the ratio K:Re = 2. It also showed that the Re–Re distances were too great to allow the existence of Re–Re bonds, which with the chemical evidence demonstrates that the solid contains discrete rhenium hydride anions. This result eliminated one of the possible explanations for the lack of temperature-dependent paramagnetism.[9]

The present paper reports a neutron diffraction study of single crystals of potassium rhenium hydride. This completely resolves the problem of its structure and composition. The results show unequivocally that the compound contains *nine* hydrogens per rhenium: six H at the corners of a trigonal prism with the Re at its center and three H beyond the centers of the rectangular prism faces (point group symmetry D_{3h}). The revised stoichiometry, K_2ReH_9, has been confirmed by thermal decomposition and combustion analyses. The magnetic properties previously reported,[9] as well as the optical spectrum of the hydride which we present in this paper, are now easily understood since an unpaired spin is no longer required by the formula. A discussion of the bonding in K_2ReH_9 is also given from the point of view of LCAO–MO theory.

Experimental

Potassium rhenium hydride was prepared as described previously.[7] The single crystals of anhydrous K_2ReH_9 were grown by slow evaporation of an aqueous KOH solution of the compound.

Crystal Data.—Potassium rhenium hydride, K_2ReH_9; formula weight 273.49; d_m 3.07 g. cm.$^{-3}$; d_x 3.094 g. cm.$^{-3}$. Hexagonal, with $a = 9.607 \pm 5$ and $c = 5.508 \pm 5$ Å.[10,11] Three formula weights per unit cell. Most probable space group, D^3_{3h}-P$\bar{6}$2m.[10] Absorption coefficient for $\lambda = 1.032$ Å. neutrons, 0.364 cm.$^{-1}$. Volume of the unit cell, 440.24 Å.^{3}. Nuclear scattering lengths, $b_{Re} = 0.92$, $b_K = 0.35$, $b_H = -0.378$ (10^{-12} cm.).

Neutron Diffraction.—Two crystals were used in the neutron diffraction investigation. Both exhibited irregular hexagonal prism development. For measurement of $I(hk0)$, the crystal had idealized dimensions 2.9 × 3.4 × 5.7 mm. with a volume of 26.8 mm.^{3}; for $I(h0l)$, the crystal had idealized dimensions 2.2 × 2.4 × 3.4 mm. with a volume of about 10.1 mm.^{3}. The intensities of the diffracted neutron beams in both zones were measured with our single crystal automatic neutron diffractometer,[12] at Brookhaven National Laboratory. K_2ReH_9 crystals are unstable in moist air, and they were preserved for the long measurement times within an evacuated goniometer-mounted cryostat[13] maintained at room temperature.

Each accessible form of every reflection was measured at least once, many being repeatedly measured, in order to establish good mean intensity values and corresponding standard deviations. A total of 46 out of 68 possible independent $hk0$ reflections and 47 out of 111 possible $h0l$ reflections were measured, within the limit of $(\sin \theta)/\lambda = 0.84$ Å.$^{-1}$ for $\lambda = 1.032$ Å. The integrated intensities were evaluated by stepping along the central lattice line through each reciprocal lattice point and counting for a predetermined monitor count of the monochromatized beam at each 0.1° 2θ interval. The background was determined by taking the average neutron count over a 1° 2θ interval

on either side and clear of the "tail" of the peak. Maximum to minimum integrated intensities in the two zones were in the ratio of 245:1 for $hk0$ and 136:1 for $h0l$. These relatively small ratios, and the large number of unobserved reflections, are caused by the large spin-incoherent cross section for hydrogen of 81 barns. The bound coherent cross section for hydrogen, by comparison, is 1.8 barns. The incoherent scattering results in high background counts and hence greatly reduces the usual signal to noise ratio.

The standard deviation in each intensity was obtained from the variation within the form of each reflection and the mean intensity value. The standard deviation in unobserved intensity terms was taken as one-half the estimated upper limit of the term. The largest differences in absorption correction are about 5% and were regarded as sufficiently small to be negligible. The mean intensity of each reflection was corrected by the Lorentz factor. The resulting structure factors, scaled to the final set of calculated structure factors, are given in Table I under F_{measd}. In this table, mean values are given for the common $F(h00)$ terms.

The $(h0l)$ layer was also carefully examined at 4.2°K. for evidence of possible magnetic scattering. No magnetic reflections were observed. The ratio of I(nuclear) at 4.2°K. to I(nuclear) at 298°K. was generally as large as 1.4:1, with many previously unobserved $I(h0l)$ clearly measurable above background.

Chemical.—Several single crystals of the hydride were washed with methanol and then with ether. After being blown dry (N_2) they were crushed to a powder in an argon-filled drybox. The powder was dried overnight *in vacuo* at 82°. All of the following experiments were performed on the dried powder. Infrared spectra (Nujol mull and KBr disk) showed the presence of small amounts of perrhenate. In order to determine the amount of $KReO_4$ in the sample a series of KBr disks was prepared containing known concentrations of $KReO_4$ over the range 0.004 to 0.125%. For each concentration three disks were produced using the same weight of KBr–$KReO_4$ mixture and applying the same pressure for the same length of time. As a check on the reproducibility of the pressing conditions, the thickness of each disk was measured with a micrometer, and corrections were made for the small variations. The peak height of the band at 915 cm.$^{-1}$, characteristic of perrhenate,[7] was determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. A plot of mean peak height *vs.* concentration of $KReO_4$ was linear over the range of 0.004 to 0.030% (4 points); at the higher concentrations the plot deviated from linearity. The perrhenate content of the hydride was now determined by preparing KBr disks of the standard thickness containing known amounts of K_2ReH_9. They gave a 915 cm.$^{-1}$ peak whose height fell on the linear portion of the calibration curve. The total rhenium content of the hydride was determined as described before.[7]

To determine the amount of hydrogen in the hydride, ~30-mg. samples were weighed into a quartz tube (28 cm. long, 12 mm. o.d.) whose top was the inner part of a 12/30 ground glass joint. The tube was connected by a ground glass cap through a three-way stopcock to a closed-end manometer reading from 0 to 260 mm. The entire system was evacuated; then the hydride was heated to redness, cooled to room temperature, and the manometer reading taken. This procedure was repeated until there was no change in the final pressure reading. The amount of hydrogen evolved was calculated from the previously determined volume of the entire system. At the conclusion of the experiment the gas evolved was transferred to an evacuated sample tube and analyzed mass spectrometrically. The volume of the system (~44 ml.) with the sample size used resulted in final pressure readings of ~190 mm.

The optical spectrum of solutions of K_2ReH_9 in 2 M CO_3^{-2}-free KOH was measured from 1400 to 210 mμ on a Cary Model 14 spectrophotometer. The final spectra were obtained from a 3.44 × 10^{-3} M solution of K_2ReH_9 in a 1-mm. path length cell with pure solvent in the reference beam. To confirm that the absorption observed was not due to impurity, the spectra of all impuri-

(10) K. Knox and A. P. Ginsberg, *Inorg. Chem.*, **3**, 555 (1964).

(11) Throughout this paper, the value of the error corresponds to the last significant digit in the function value.

(12) E. Prince and S. C. Abrahams, *Rev. Sci. Instr.*, **30**, 581 (1959).

(13) S. C. Abrahams, *ibid.*, **31**, 174 (1960).

TABLE I

MEASURED AND CALCULATED VALUES OF THE K_2ReH_9 STRUCTURE FACTORS AT 298°K.

hkl	F_{measd}	$F_{calcd}{}^a$	hkl	F_{measd}	$F_{calcd}{}^a$	hkl	F_{measd}	$F_{calcd}{}^a$	hkl	F_{measd}	$F_{calcd}{}^a$
100	<0.22	0.05	830	<0.71	0.72	107	<1.25	1.17	606	<1.25	0.46
200	0.28	0.28	930	1.82	2.04	108	<1.31	0.70	607	<1.26	−0.01
300	5.38	5.41	10,3,0	<0.77	0.23	109	<1.25	0.54	608	<1.26	1.18
400	<0.63	−0.73	11,3,0	<0.77	0.23	201	3.17	2.98	701	<1.03	1.01
500	1.61	1.54	12,3,0	1.38	1.60	202	<0.69	−0.26	702	1.29	1.35
600	<0.54	−0.12	440	3.42	3.49	203	3.66	3.70	703	2.28	2.31
700	0.46	0.45	540	1.20	1.04	204	<0.83	0.18	704	<1.15	0.51
800	0.55	−0.55	640	<0.53	0.45	205	1.88	1.85	705	<1.20	0.40
900	1.55	1.58	740	2.39	2.08	206	<1.09	0.28	706	<1.27	1.04
10,0,0	<0.69	−0.37	840	0.80	0.71	207	2.04	2.28	707	<1.29	1.30
11,0,0	0.78	−0.41	940	1.14	0.81	208	<1.31	0.40	801	1.61	1.36
12,0,0	2.36	2.30	10,4,0	1.60	1.64	209	<1.24	1.38	802	<1.06	0.76
13,0,0	<0.76	−0.71	11,4,0	<0.73	0.46	301	1.72	−1.55	803	2.13	2.06
110	1.55	1.55	550	3.13	3.11	302	3.75	3.80	804	<1.17	−0.14
210	1.30	1.25	650	0.95	1.01	303	1.10	−0.78	805	<1.25	0.77
310	<0.46	0.22	750	<0.66	0.37	304	3.66	3.73	806	<1.31	0.54
410	3.72	3.74	850	1.83	1.77	305	<1.04	−1.02	807	<1.27	1.16
510	2.15	2.11	950	0.92	0.51	306	2.94	3.08	901	1.25	−1.05
610	1.48	1.55	10,5,0	<0.74	0.16	307	<1.25	−0.22	902	3.39	3.21
710	1.12	0.78	660	1.53	1.80	308	<1.30	1.99	903	<1.17	−0.66
810	1.15	1.23	760	<0.61	0.51	309	<1.23	0.09	904	1.44	1.54
910	0.98	1.26	860	<0.76	0.88	401	0.77	0.69	905	<1.31	−0.59
10,1,0	1.46	1.47	960	1.36	1.16	402	2.48	2.49	906	1.53	1.85
11,1,0	0.87	1.22	770	1.91	2.18	403	1.14	−0.98	10,0,1	1.50	1.57
12,1,0	<0.77	0.45	870	<0.75	0.13	404	<0.94	0.36	10,0,2	<1.18	0.96
13,1,0	1.02	1.12	880	<0.80	1.12	405	1.66	1.39	10,0,3	<1.25	0.95
220	5.42	5.37	001	0.66	0.79	406	<1.12	1.19	10,0,4	<1.31	0.34
320	0.90	0.81	002	6.35	6.80	407	<1.28	−0.07	10,0,5	1.30	1.28
420	3.77	3.90	003	1.13	−0.94	408	<1.29	1.03	10,0,6	<1.26	0.25
520	2.31	2.34	004	0.86	−0.77	501	1.39	1.35	11,0,1	<1.25	0.20
620	1.32	1.17	005	<1.14	1.15	502	<0.74	−0.57	11,0,2	<1.25	−0.47
720	<0.57	0.54	006	1.96	2.03	503	1.87	1.98	11,0,3	<1.25	0.68
820	1.91	1.91	007	<1.25	−0.04	504	<0.97	1.00	11,0,4	<1.25	−0.31
920	<0.70	0.65	008	1.85	1.71	505	1.41	1.02	11,0,5	<1.22	0.14
10,2,0	<0.77	0.40	009	<1.25	0.51	506	<1.18	0.40	12,0,1	<1.31	−0.62
11,2,0	1.38	1.43	101	0.69	−0.91	507	<1.31	1.31	12,0,2	1.82	1.92
12,2,0	<0.71	0.12	102	0.94	0.38	508	<1.28	0.69	12,0,3	<1.29	−0.24
330	4.47	4.14	103	1.63	1.50	601	1.35	−1.06	12,0,4	1.89	1.82
430	1.22	1.22	104	<0.85	0.28	602	1.12	1.15	13,0,1	<1.28	0.78
530	1.70	1.88	105	1.07	−0.96	603	<0.95	−1.13	13,0,2	<1.27	0.15
630	1.76	1.88	106	<1.00	0.68	604	<1.12	1.09	13,0,3	<1.26	0.69
730	1.62	1.63				605	<1.16	−0.45			

a Signs are given in this table only for those F_{calcd} terms for which $B = 0$, *i.e.*, $F(h0l)$. For $F(hk0)$, only the modulus is given.

ties which previous experience has shown might be present ($KReO_4$, K_2CO_3, KOH, and $NH_2CH_2CH_2NH_2$) were examined. None of these substances absorbed at the wave length observed for the K_2ReH_9 solution.

Results

Analysis of the Neutron Diffraction Data.—The neutron diffraction data were analyzed by a combination of Fourier series and least-squares techniques. The $hk0$ data were analyzed alone because they were measured first, and finally a combination of $hk0$ and $h0l$ reflections were used. The $hk0$ neutron scattering density projection, using phases calculated for the Re and K positions from the X-ray analysis,[10] revealed two sets of three negative peaks representing hydrogen nuclei. They were arranged around each Re in two triangles, as required by the p31m plane symmetry. Refinement by least squares, using the full-matrix program of Busing and Levy,[14] with the Re and K in the

(14) W. R. Busing and H. A. Levy, ORNL Central Files No. 59-4-37 (1959).

X-ray determined positions, six H around each of the three Re, and isotropic temperature factors, converged rapidly to weighted $R = 16\%$. At this stage, on the basis of the chemical formula being K_2ReH_8, two additional H per Re were included in the calculation, which in projection came in pairs at $0,0$; $^1/_3,^2/_3$; and $^2/_3,^1/_3$. Refinement of this model by least squares was entirely unsatisfactory; *viz.*, R increased to 26%, many calculated structure factors deviated considerably from the observed values, and several temperature factors became unreasonable (*e.g.*, B for the two H at $0,0$ increased to 55 Å.²). With the phases of the least squares for the K_2ReH_6 model, we calculated a Fourier synthesis of the projected neutron scattering density. It revealed again two sets of three negative peaks around each Re, with one set closer in and considerably more negative (almost twice the depth of the other). These larger negative peaks, in the cases of both crystallographically different Re, were directed toward the K atoms in the plane of the Re. Thus, at this stage it

TABLE II
FINAL ATOMIC COORDINATES FOR K_2ReH_9

Atom	x	y	z	β_{11}	β_{22}
Re_1	0	0	0	0.0061 ± 9	b
Re_2	$1/3$	$2/3$	$1/2$	0.0034 ± 4	b
K_1	0.5881 ± 14	0	0	0.0035 ± 9	0.0050 ± 17
K_2	0.2610 ± 29	0	$1/2$	0.0173 ± 37	0.0076 ± 25
H_1	0.1789 ± 24	0	0	0.0112 ± 16	0.0134 ± 40
H_2	0.8789 ± 14	0	0.2171 ± 32	0.0190 ± 19	0.0080 ± 13
H_3	0.1483 ± 18	0.6250 ± 24	$1/2$	0.0187 ± 37	0.0189 ± 25
H_4	0.2240 ± 10	0.5254 ± 13	0.7125 ± 20	0.0151 ± 13	0.0145 ± 15

Atom	β_{33}	β_{12}	β_{13}	β_{23}	$B,^a$ Å.^{2}
Re_1	0.0004 ± 55	b	0	0	1.44 ± 17
Re_2	0.0153 ± 43	b	0	0	1.01 ± 9
K_1	0.0207 ± 94	c	0	0	0.84 ± 19
K_2	0.0105 ± 80	c	0	0	3.55 ± 43
H_1	0.0260 ± 116	c	0	0	2.47 ± 25
H_2	0.0354 ± 62	c	0.0081 ± 72	0	4.21 ± 22
H_3	0.0198 ± 50	0.0120 ± 27	0	0	3.46 ± 25
H_4	0.0363 ± 39	0.0080 ± 11	0.0120 ± 48	0.0086 ± 47	4.15 ± 19

^{a} These values of B are from the last cycle of least-squares refinement with isotropic temperature factors. ^{b} $\beta_{11} = \beta_{22} = 2\beta_{12}$. ^{c} $\beta_{22} = 2\beta_{12}$

appeared that there should be nine H per Re, six arranged in a trigonal prism with three more beyond the centers of the three rectangular prism faces. This model fits inside the space left by the nine K neighbors of each Re most effectively on a stereochemical basis; it is proved by the final result of the refinement of the diffraction data. The possibility of eight H per Re, arranged six in a trigonal prism with two H beyond two of the three rectangular faces in a disordered crystal array, was ruled out by allowing the occupancy factor of each of the hydrogens to vary. The effective number of nuclei at each site, after refinement, deviated by less than three standard deviations (mostly much less than that) from the expected values for K_2ReH_9. Several other possible models, including the one in which two hydrogen nuclei were placed at the smaller rather than the larger negative peaks in the $hk0$ projection, were also investigated, but none gave nearly as satisfactory a fit as the one finally chosen. The chemical formula is then K_2ReH_9, as has been verified by subsequent chemical analysis; *vide infra.*

The trial structure for K_2ReH_9 in space group D^3_{3h}-$P\bar{6}2m$ is

1 Re_1 in 1(a): 000
2 Re_2 in 2(d): $\pm 1/3 \cdot 2/3 \cdot 1/2$
3 K_1 in 3(f): $x00$, etc., with $x \approx 0.6$
3 K_2 in 3(g): $x0 1/2$, etc., with $x \approx 0.25$
3 H_1 in 3(f): $x00$, etc., with $x \approx 0.2$
6 H_2 in 6(i): $x0z$, etc., with $x \approx 0.9$, $z \approx 0.2$
6 H_3 in 6(k): $xy 1/2$, etc., with $x \approx 0.15$, $y \approx 0.6$
12 H_4 in 12(l): xyz, etc., with $x \approx 0.2$, $y \approx 0.5$, $z \approx 0.7$

These coordinates were refined by least squares, first using the $hk0$ and $h0l$ data separately with isotropic and then with anisotropic thermal parameters; finally the two zones were refined together with isotropic and then anisotropic thermal parameters. Separate scale factors were used for each zone. The final positional parameters in all of these refinements never varied by more than three standard deviations from one set to an-

other, and most of them agreed within one standard deviation. In the final least squares analysis of the $hk0$ and $h0l$ zones together, β_{33} of Re_1 became negative and converged to a value less than two standard deviations from zero. To get meaningful results for the bond-distance calculation given below, this β was given a positive value, which in the last least-squares cycle refined to a very small positive number. In this cycle none of the positional parameters changed by as much as one-half of their standard deviations (σ) and none of the other β values by more than 1.5σ. The results of this last cycle are given in Table II, along with the final set of isotropic temperature factors (the maximum difference in positional coordinate is 2σ for x_{H_2} and y_{H_3}; all other differences are less than σ). The weighted R after this cycle is 7.7%, while the conventional $R = 8.6\%$. The calculated structure factors from this final anisotropic temperature factor refinement are given in Table I under F_{calcd}. After complete refinement with isotropic temperature factors, the weighted R was 9.1%. The positions of the potassium ions from the neutron diffraction data are within 3σ of the positions determined by X-ray diffraction.[10] The (001) projection of the neutron scattering density is shown in Fig. 1.

Chemical Analysis.—On heating the hydride to red heat, a bright film of potassium metal formed in the cool part of the tube, and a black residue presumably (Re metal) remained in the bottom. A thin brown film was also observed in the lower part of the tube. Mass spectrometric analysis of the evolved gas gave the results in Table III.

The presence of methane in gas indicates an organic impurity in the hydride which, from the method of preparation,[7] could only be ethylenediamine. A C, H determination by combustion analysis (Schwarzkopf Microanalytical Laboratory) gave: *Anal.* Found: C, 0.48, 0.42; H, 3.18, 3.39. This carbon content corresponds to 1.12% ethylenediamine in the hydride. The total rhenium analysis gave 67.44% Re; the
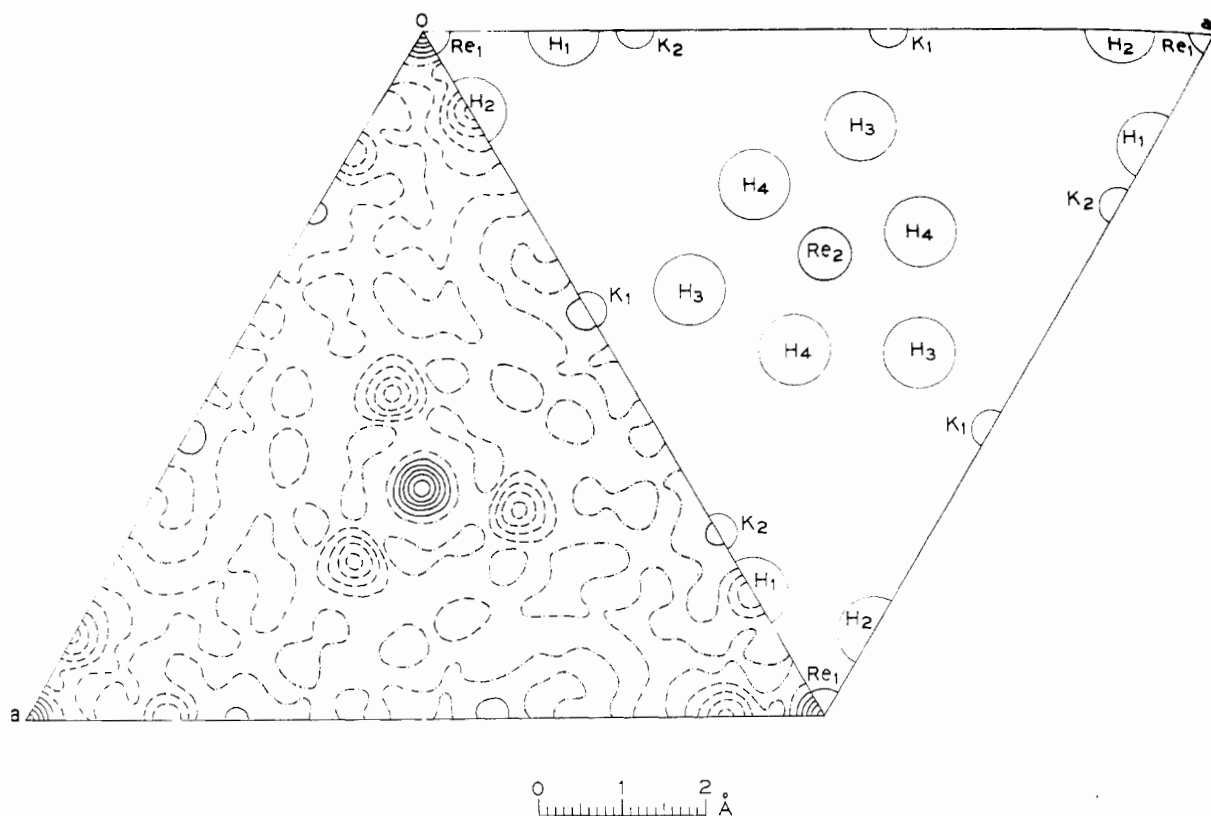
Fig. 1.—Neutron scattering density of K_2ReH_9 projected along the c-axis, at 298°K. Contours are at intervals of 10^{-12} cm. Å.$^{-2}$, except for the negative contours where the interval is 0.5×10^{-12} cm. Å.$^{-2}$. The zero contour is a dot–dash, the negative contours dashed lines.

infrared perrhenate determination gave 2.33% Re present as ReO_4^- (3.62% $KReO_4$ contaminant). There is then 65.11% Re present as hydride; *i.e.*, the hydride is 96.5% pure.   From the last result and the amount of hydrogen in the gas (99.3%), the pressure readings give the first two values in Table IV for the H:Re ratio.   The second pair of values in Table IV was obtained from the combustion analysis after correction for the hydrogen due to ethylenediamine (0.15%).

<div align="center">

TABLE III

MASS SPECTROMETRIC ANALYSIS OF GAS EVOLVED ON THERMAL DECOMPOSITION OF K_2ReH_9

</div>

Substance	% by volume
CO_2	0.001
Ar	0.011
O_2	0.0003
CO	0.036
N_2	0.304
H_2O	0.043
CH_4	0.239
H_2	99.27
Total	99.91

<div align="center">

TABLE IV

H:Re RATIO BY THERMAL DECOMPOSITION AND COMBUSTION ANALYSIS

</div>

Method	Moles H per mole Re
Thermal decomposition	8.70
Thermal decomposition	8.67
Combustion	8.60
Combustion	9.20

In view of the presence of small amounts of impurities and the difficulty of the analysis (one H corresponds to 0.37%) these results are in satisfactory agreement with the H:Re ratio of 9 required by the neutron diffraction analysis.

Optical Spectrum.—The optical spectrum of K_2ReH_9 in aqueous KOH showed only a single absorption with a maximum at 46,080 cm.$^{-1}$ and a molar extinction coefficient ϵ_{max} 1.8×10^3. The slit of the spectrophotometer was wide open at 47,600 cm.$^{-1}$ so that only part of the high energy side of the band could be recorded.   The band appeared to be gaussian in shape and had a half-width $\delta = 3590$ cm.$^{-1}$.   The oscillator strength is therefore $f = 4.60 \times 10^{-9} \times \epsilon_{max} \times \delta = 2.98 \times 10^{-2}$.

<div align="center">

Discussion

</div>

Internuclear Distances and Angles at 298°K.—The positional coordinates from the final least-squares refinement cycle, given in Table II, together with the lattice constants in the Crystal Data section, lead to the distances and angles in Table V.   These values, with their standard deviaitons, were computed using the Busing and Levy ORFFE program[15] for the IBM 7090 computer.   The correlation matrix from the final least-squares cycle was used in the error calculation.   In this table, no allowance has been made for thermal vibrations.

(15) W. R. Busing and H. A. Levy, ORNL Central Files No. 59-12-3 (1959).

TABLE V

HYDROGEN DISTANCES LESS THAN 4 Å.[a] AND ANGLES IN K_2ReH_9

	Distance, Å.		Distance, Å.
Re_1–H_1 (3)	1.72 ± 2	Re_2–H_3 (3)	1.61 ± 2
Re_1–H_2 (6)	1.67 ± 2	Re_2–H_4 (6)	1.70 ± 1
H_1–H_1 (2)	2.98 ± 4	H_3–H_3 (3)	2.80 ± 3
H_1–H_2 (4)	1.93 ± 2	H_3–H_4 (2)	1.874 ± 15
H_1–K_1 (2)	3.44 ± 1	H_3–H_4 (2)	1.872 ± 16
H_1–K_1 (1)	3.93 ± 3	H_3–K_1 (2)	3.04 ± 1
H_1–K_2 (2)	2.86 ± 1	H_3–K_2 (1)	3.05 ± 3
		H_3–K_2 (1)	3.20 ± 2
H_2–H_2 (2)	2.02 ± 2	H_4–H_4 (2)	2.15 ± 2
H_2–H_2 (1)	2.39 ± 2	H_4–H_4 (1)	2.75 ± 3
		H_4–K_1 (1)	2.97 ± 1
H_2–K_1 (1)	3.04 ± 2	H_4–K_1 (1)	2.99 ± 1
H_2–K_2 (2)	2.67 ± 2	H_4–K_2 (1)	2.64 ± 2

Angles

H_2–Re_1–H_2	$91.6 \pm 1.1°$
H_4–Re_2–H_4	$95.6 \pm 0.5°$

H_3–Re_2–H_4 projected along trigonal axis onto (001) = $59.1 \pm 1.0°$

[a] With no allowance for thermal motions. Parenthetical values are the number of contacts.

Since the Re_1–$6H_2$–$3H_1$ ion is crystallographically independent of Re_2–$6H_4$–$3H_3$, the distances corresponding to each ion are listed in separate columns in Table V. The crystallographically nonequivalent ReH_9^{-2} ions, based on Re_1 and Re_2, not only possess essentially the same dimensions, but also very nearly the same environment. The site symmetry of Re_2 is C_{3h}-$\bar{6}$, but within experimental error it is D_{3h}-$\bar{6}m2$ as can be seen from the projected H_3–Re_2–H_4 angle in Table V, which is not significantly different from 60°. It is to be noted that the steric arrangement of the ReH_9^{-2} ion is such as to fill the interstices in the Re and K atom structure with maximum packing efficiency (see Fig. 2).

The large thermal nuclear vibrations, shown in Table VII, may also be considered in computing the internuclear distances. This has been done using two assumptions: (a) that the H atom "rides" on the Re nuclear motion, and (b) that the motion of the H atom is independent of the Re atom motion. The Re–H distances, based on each of these two assumptions, are given in Table VI, together with those assuming stationary atoms for comparison. It is seen that these assumptions lead to greater Re–H distances, as expected, but the doubtful validity of the assumptions leads us to use the values in the first column.

Amplitudes of Thermal Vibration.—The amplitudes of thermal vibration can readily be computed from the β_{ij} values in Table II, using Busing and Levy's program ORFFE.[15] The amplitudes along the princi-

TABLE VI

Re–H DISTANCES (Å.) IN ReH_9^{-2}

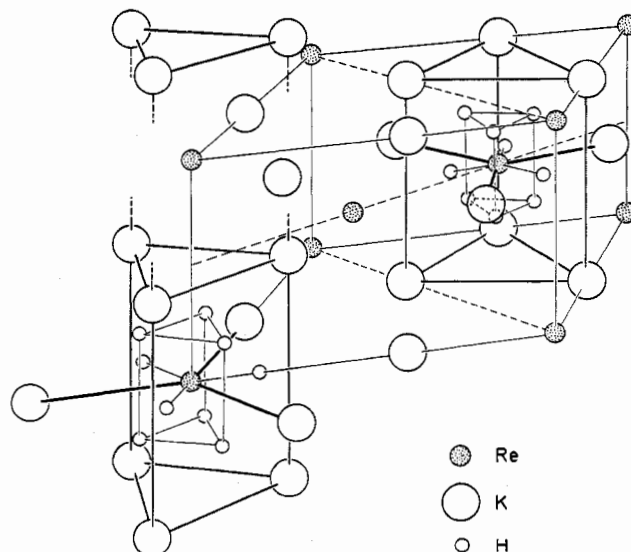|	Stationary atoms	H riding on Re	Independent motions
Re–H_1	1.72	1.74	1.75
Re–H_2	1.67	1.69	1.71
Re–H_3	1.61	1.63	1.65
Re–H_4	1.70	1.73	1.75
Av. Re–H	1.68	1.70	1.72

Fig. 2.—Arrangement of atoms in the unit cell of K_2ReH_9.

pal axes of the ellipsoid of thermal vibration are not reproduced in this paper, but the root mean square radial thermal displacement of each nucleus is given in Table VII.

TABLE VII

ROOT MEAN SQUARE RADIAL THERMAL DISPLACEMENTS

Atom	Radial displacement, Å.
Re_1	0.21 ± 2
Re_2	0.22 ± 2
K_1	0.24 ± 3
K_2	0.34 ± 3
H_1	0.35 ± 4
H_2	0.40 ± 2
H_3	0.39 ± 2
H_4	0.40 ± 1

These values may be compared with the nuclear radial displacements[16] in $CuF_2·2H_2O$ at 298°K. of 0.20 $\pm$ 1 Å. for Cu^{2+} (atomic number 29 vs. 19 for K and 75 for Re) and 0.26 $\pm$ 2 Å. for H.

LCAO–MO Description.—The reducible representation for the Re–H bonds in the ReH_9^{-2} ion may be decomposed as follows into irreducible representations

$$\Gamma(\text{Re–H}) = 2A_1' + 2E' + A_2'' + E''$$

This is precisely the sum of the irreducible representations of the 5d, 6s, and 6p orbitals in the point group D_{3h}; hence all of these orbitals are used in forming bonds with hydrogen. From the point of view of Pauling's theory the bonding scheme can therefore be described as resulting from d^5sp^3 hybridization.

The normalized linear combinations of ligand hydrogen 1s orbitals which have the proper transformation properties to combine with the rhenium atomic orbitals are given in Table VIII, which also lists the transformation properties of the rhenium AO's in D_{3h} symmetry. The numbering scheme for the hydrogens is shown in Fig. 3. A right-handed coordinate system is used with the origin at the Re, the z-axis vertical, and

(16) S. C. Abrahams and E. Prince, *J. Chem. Phys.*, **36**, 50 (1962).
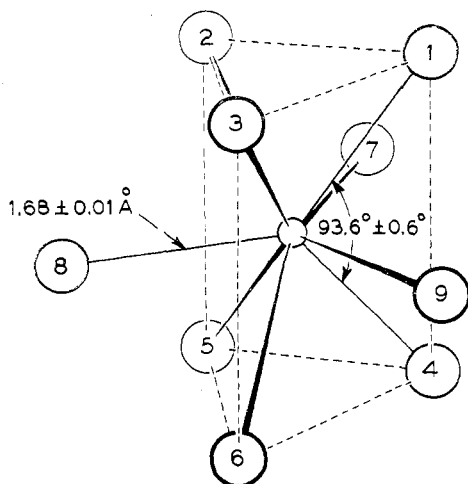
Fig. 3.—Perspective arrangement of hydrogen atoms in ReH$_9^{2-}$. Atoms 1–6 are the prism, atoms 7–9 the equatorial hydrogens.

the $-x$-axis passing through H$_8$. χ_i is the 1s AO of hydrogen atom H$_i$. Since there is no symmetry operation in D$_{3h}$ which transforms an equatorial H into a prism H, certain of the irreducible representations are spanned by *two* linearly independent combinations of H 1s orbitals: one combination is composed entirely of prism hydrogens, the other entirely of equatorial hydrogens. In obtaining the normalization constants for the ligand symmetry orbitals, H–H overlap was neglected.

TABLE VIII

LIGAND SYMMETRY ORBITALS AND METAL AO TRANSFORMATION PROPERTIES IN D$_{3h}$ SYMMETRY

Representation	Re AO	Ligand orbitals
a$_1'$	5d$_{z^2}$,6s	$\Phi_1 = \frac{1}{\sqrt{6}}\{\chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5 + \chi_6\}$
		$\Phi_2 = \frac{1}{\sqrt{3}}\{\chi_7 + \chi_8 + \chi_9\}$
a$_2''$	6p$_z$	$\Phi_3 = \frac{1}{\sqrt{6}}\{\chi_1 + \chi_2 + \chi_3 - \chi_4 - \chi_5 - \chi_6\}$
e$'$	5d$_{x^2-y^2}$,5d$_{xy}$	$\Phi_4 = \frac{1}{2\sqrt{3}}\{\chi_2 + \chi_3 + \chi_5 + \chi_6 - 2\chi_1 - 2\chi_4\}$
		$\Phi_5 = \frac{1}{2}\{\chi_3 + \chi_6 - \chi_2 - \chi_5\}$
	6p$_x$,6p$_y$	$\Phi_6 = \frac{1}{\sqrt{6}}\{\chi_7 + \chi_8 - 2\chi_9\}$
		$\Phi_7 = \frac{1}{\sqrt{2}}\{\chi_7 - \chi_8\}$
e$''$	5d$_{xz}$,5d$_{yz}$	$\Phi_8 = \frac{1}{2\sqrt{3}}\{2\chi_4 + \chi_2 + \chi_3 - 2\chi_1 - \chi_5 - \chi_6\}$
		$\Phi_9 = \frac{1}{2}\{\chi_2 + \chi_5 - \chi_3 - \chi_6\}$

To go further with the MO description it is necessary to choose explicit basis functions for the rhenium and hydrogen orbitals. The simplest orbitals to use are Slater's with the effective nuclear charge given by Slater's rules.[17] Although this procedure is, of course,

(17) See, for example, H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, New York, N. Y., 1954, p. 162.

TABLE IX

GROUP OVERLAP INTEGRALS FOR Re 5d ORBITALS WITH H 1s ORBITALS

Ligand symmetry orbital	Metal AO	Group overlap integral	
		$\mu_a = 0.7$ $\mu_b = 1.75$	$\mu_a = 0.933$ $\mu_b = 1.40$
Φ_1	5d$_{z^2}$	0.1851	0.2694
Φ_2	5d$_{z^2}$	−0.2618	−0.3811
Φ_4	5d$_{x^2-y^2}$	−0.2267	−0.3300
Φ_6	5d$_{x^2-y^2}$	−0.3205	−0.4665
Φ_5	5d$_{xy}$	0.2267	0.3300
Φ_7	5d$_{xy}$	0.3205	0.4665
Φ_8	5d$_{xz}$	−0.4534	−0.6420
Φ_9	5d$_{yz}$	0.4534	0.6420
$\frac{1}{\sqrt{3}}(\Phi_1 - \sqrt{2}\Phi_2)$	5d$_{z^2}$	0.3206	0.4667
$\frac{1}{\sqrt{3}}(\Phi_4 + \sqrt{2}\Phi_6)$	5d$_{x^2-y^2}$	−0.3926	−0.5714
$\frac{1}{\sqrt{3}}(\Phi_5 + \sqrt{2}\Phi_7)$	5d$_{xy}$	0.3926	0.5714

very crude it leads to results which are at least of qualitative significance. Let μ_a and μ_b be the Slater orbital exponents for hydrogen and rhenium, respectively. Consider the rhenium hydride anion from two extreme points of view. (1) Suppose it to be made up of Re^{+7} plus nine H$^-$. Then Slater's rules give $\mu_a = Z_{eff}(H^-) = 0.7$; $\mu_b = Z_{eff}(Re^{+7})/4.00 = 1.75$. (2) Suppose it to consist of Re^0 plus nine H$^{-2/9}$. Slater's rules then give $\mu_a = Z_{eff}(H^{-2/9}) = 0.933$ and $\mu_b = Z_{eff}(Re^0 (5d))/4.00 = 1.40$. Using the procedure described by Mulliken, *et al.*,[18] and the tables of A and B integrals given by Miller, Gerhauser, and Matsen,[19] the values of the group overlap integrals obtained are listed in Table IX. In making the calculation all Re–H distances were taken to be 1.67 Å, and the acute angle between the z-axis and a Re–H prism direction to be 45° (*cf.* Fig. 3).

To find the *total* overlap for the 5d$_{z^2}$, 5d$_{x^2-y^2}$, and 5d$_{xy}$ orbitals it is necessary to know the relative weights with which the two linearly independent symmetry orbitals enter the molecular orbital. We will assume that the ratio of the mixing coefficients for the equatorial hydrogen symmetry orbital to the prism hydrogen symmetry orbital is given by the ratio of the corresponding group overlap integrals. From Table IX, this ratio is $-\sqrt{2}$ for overlap with the 5d$_{z^2}$, $+\sqrt{2}$ for overlap with the 5d$_{x^2-y^2}$, and $+\sqrt{2}$ for overlap with the 5d$_{xy}$ orbital (independent of the effective nuclear charge). The complete normalized ligand MO's for overlap with 5d$_{z^2}$, 5d$_{x^2-y^2}$, and 5d$_y$ are therefore, respectively

$$\frac{1}{\sqrt{3}}(\Phi_1 - \sqrt{2}\Phi_2)$$

$$\frac{1}{\sqrt{3}}(\Phi_4 + \sqrt{2}\Phi_6)$$

$$\frac{1}{\sqrt{3}}(\Phi_5 + \sqrt{2}\Phi_7)$$

(18) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(19) J. Miller, J. Gerhauser, and F. A. Matsen, "Quantum Chemistry Integrals and Tables," University of Texas Press, Austin, Texas, 1958.
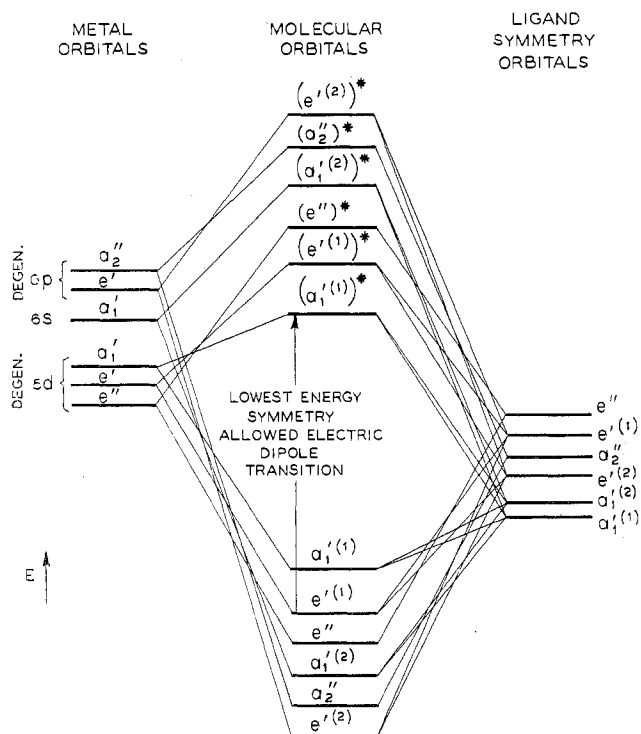
Fig. 4.—Molecular orbital energy level scheme for ReH_9^{-2} based on overlap considerations.

The group overlap integrals for these MO's are listed in the last three lines of Table IX. The group overlap integrals with the 6s and 6p orbitals cannot be evaluated by the procedure of ref. 18. We assume that they are greater in magnitude than any of the integrals in Table IX and that the resulting bonding MO's are lower in energy than any of those involving the 5d orbitals.[20] The correlation diagram in Fig. 4 portrays the relative ordering of the MO energies for ReH_9^{-2} assuming the relative energies of the bonding orbitals and the relative energies of the antibonding orbitals are proportional to the magnitude of the group overlap integral. The relative positions of the free atom metal and ligand orbitals in Fig. 4 are completely arbitrary and without significance.

We assign the band observed in the optical spectrum to the energetically lowest symmetry allowed electric dipole transition.[21] Then, with the ordering of the MO energies depicted in Fig. 4, it corresponds to the transition $e'^{(1)} \rightarrow (a_1'^{(1)})^*$ indicated in the figure. (The $a_1'^{(1)} \rightarrow (e'^{(1)})^*$ transition is more energetic because the $(e'^{(1)})^*$ orbital is more strongly antibonding than the $e'^{(1)}$ orbital is bonding.) The assignment of the observed 46,080 cm.$^{-1}$ band to a transition between bonding and antibonding orbitals shows that the splitting between these orbitals is quite large. This is in agreement with the finding of Chatt and Hayter[22] that hydrogen in transition metal complexes has a large ligand field strength.

(20) This appears to be the usual situation: *cf.* C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, pp. 61–62; A. D. Liehr, *J. Chem. Educ.*, **39**, 135 (1962).

(21) We assume the same structure for ReH_9^{-2} in solution as has been found by neutron diffraction in the solid.

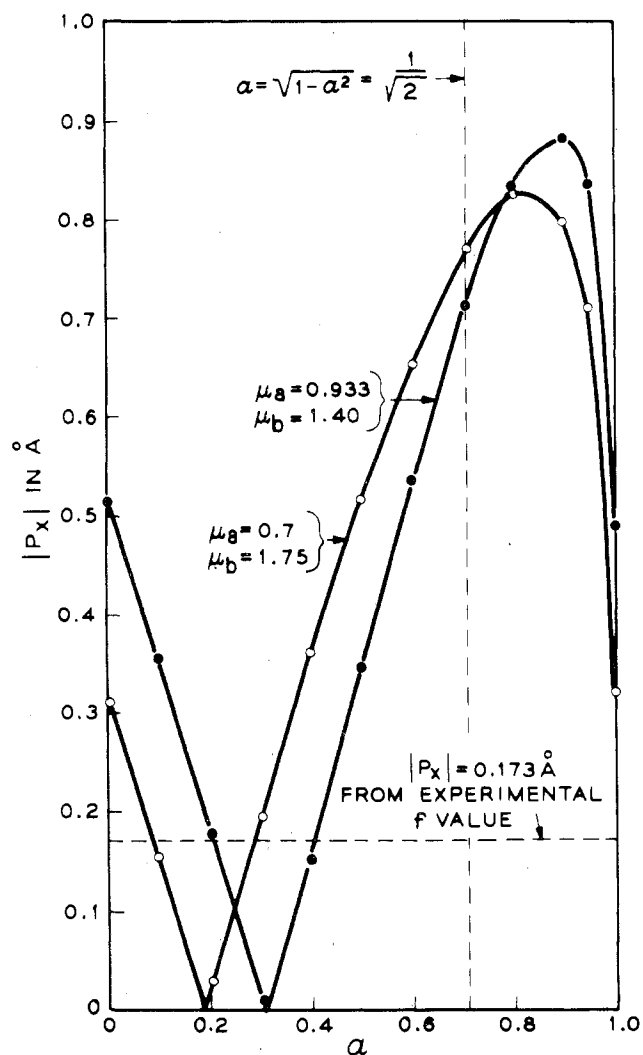(22) J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 772 (1961).

Fig. 5.—Plot of theoretical equation relating $|P_x|$ to the MO mixing coefficient α.

The intensity of the ultraviolet absorption may be used to obtain a rough idea of the polarity of some of the rhenium–hydrogen molecular orbitals.[23] With the assumption that the ligand–metal mixing coefficient for the $a_1'^{(1)}$ MO is the same as for the two $e'^{(1)}$ orbitals, the MO's between which the observed transition takes place may be written as given below

$$\Psi(e_a'^{(1)}) = \alpha\Psi(5d_{x^2-y^2}) - \sqrt{1-\alpha^2}\left\{\frac{1}{\sqrt{3}}(\Phi_4 + \sqrt{2}\Phi_6)\right\}$$

$$\Psi(e_b'^{(1)}) = \alpha\Psi(5d_{xy}) + \sqrt{1-\alpha^2}\left\{\frac{1}{\sqrt{3}}(\Phi_5 + \sqrt{2}\Phi_7)\right\}$$

$$\Psi(a_1'^{(1)})^* = \sqrt{1-\alpha^2}\,\Psi(5d_{z^2}) - \alpha\left\{\frac{1}{\sqrt{3}}(\Phi_1 - \sqrt{2}\Phi_2)\right\}$$

where the contribution of the metal–ligand overlap to the normalization constant has been neglected. The components of the transition moment integral are given by

$$P_x = \sqrt{2}\langle\Psi(e_a'^{(1)})|\vec{r}|\Psi(a_1'^{(1)})^*\rangle\cdot\vec{i}$$

$$P_y = \sqrt{2}\langle\Psi(e_b'^{(1)})|\vec{r}|\Psi(a_1'^{(1)})^*\rangle\cdot\vec{j}$$

$$P_z = 0$$

(23) C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectry.*, **2**, 342 (1958); **4**, 190 (1960); C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, p. 170.

Noting that $\int \Psi(5d_{x^2-y^2})\Psi(5d_{z^2})\vec{r}d\tau = \int \Psi(5d_{xy})\Psi(5d_{z^2}) \cdot \vec{r}d\tau = 0$, and making the approximation $\int \chi_i\chi_j\vec{r}d\tau \cdot \vec{i} = \delta_{ij}x_{Re-H}$ and $\int \chi_i\chi_j\vec{r}d\tau \cdot \vec{j} = \delta_{ij}y_{Re-H}$, where x_{Re-H} and y_{Re-H} are the x and y components of the Re–H distance, we get by straightforward calculation that: For $\mu_a = 0.7$, $\mu_b = 1.75$

$$P_x = -P_y = (0.3110 - 0.6112\alpha^2 - 1.5070\alpha\sqrt{1-\alpha^2}) \text{ Å}.$$

For $\mu_a = 0.933$, $\mu_b = 1.40$

$$P_x = -P_y = (0.5166 - 1.0595\alpha^2 - 1.5070\alpha\sqrt{1-\alpha^2}) \text{ Å}.$$

The relation

$$f = 1.085 \times 10^{-5}\nu_{max}[P_x^2 + P_y^2 + P_z^2]$$

together with the experimental value of the oscillator strength, leads to $|P_x| = |P_y| = 0.173$ Å. Figure 5 shows a plot of $|P_x|$ *vs.* α as given by the theoretical equations; the horizontal line represents the value of $|P_x|$ calculated from the experimental oscillator strength, while the vertical line marks $\alpha = 1/\sqrt{2}$, *i.e.*, the value for a nonpolar MO. From Fig. 5 we can draw the qualitative conclusion that the $a_1'^{(1)}$, $e_a'^{(1)}$, and $e_b'^{(1)}$ orbitals are polarized toward the hydrogen since all possible values of α are much less than $1/\sqrt{2}$. This indicates that the description of some transition metal hydrides as having protons buried in the metal d-electron density[24] (to explain the high-field proton resonance shift) is not applicable to K_2ReH_9. Recent theoretical work[25] also shows that this description is really not necessary to account for the large n.m.r. shift of HCo-(CO)$_4$ and analogous compounds.

In this connection we note that the Re–H distance in K_2ReH_9 is considerably greater than Pauling's single bond metallic radius (1.28 Å.) of the rhenium atom and is consistent with the ordinary radii sum rules. On the other hand, in $H_2Fe(CO)_4$ the Fe–H distance of 1.1 Å., estimated from the broad line n.m.r. spectrum,[26] is slightly less than Pauling's metallic radius of Fe (1.16 Å.) and is in disagreement with any normal radius sum. A similar Mo–H distance of 1.1 Å. has been inferred in $(C_5H_5)_2MoH_2$, on the basis of a two-dimensional X-ray study.[27] This distance is less than the metallic radius of Mo and is considerably less than a normal radius sum. In contrast, a preliminary report of a three-dimensional X-ray analysis of HRh(CO)(P-(C$_6$H$_5$)$_3$)$_3$ claims[28] to have located the hydridic hydrogen at a normal Rh–H distance of 1.72 ± 0.15 Å. In comparing these various results it should be recalled that the neutron diffraction method is intrinsically superior to the X-ray method in determination of hydrogen atom positions in the presence of high atomic number elements.

Within the framework of the LCAO–MO theory neglecting configuration interaction, the principal

(24) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 4425 (1958).

(25) R. M. Stevens, C. W. Kern, and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 279 (1962).

(26) E. O. Bishop, J. L. Down, P. R. Emtage, R. E. Richards, and G. Wilkinson, *J. Chem. Soc.*, 2484 (1954).

(27) M. J. Bennett, M. Gerloch, J. A. McCleverty, and R. Mason, *Proc. Chem. Soc.*, 357 (1962).

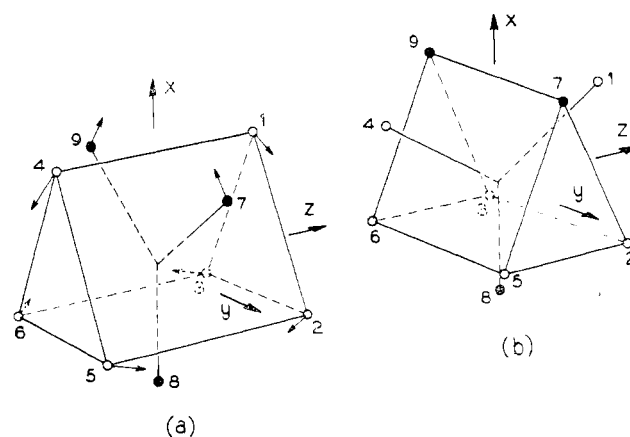(28) S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, **85**, 3501 (1963).

(a)

(b)

Fig. 6.—One component of a deformation mode of symmetry E' which can interchange prism and equatorial hydrogens.

source of error in the MO calculation is the use of Slater orbitals for the rhenium. The sensitivity of the conclusion about the direction of polarity of the MO's, based on the value of α, to the evaluation of the integrals involving the rhenium orbitals can be tested by choosing different values for those integrals. Doubling the integrals shifts the intersections of the curves of Fig. 5 with the line representing the experimental value of $|P_x|$ by ~ 0.1 to higher values of α. The qualitative conclusion about the polarity of the orbitals would therefore remain unchanged. Halving the integrals shifts both curves in Fig. 5 so that their intersections with the line of experimental $|P_x|$ occur at values of α lower by ~ 0.1, again leaving the conclusion unchanged. However, for the case $\mu_a = 0.7$, $\mu_b = 1.75$, the value $\alpha = 0.9999$ (the curve is practically vertical in this region) *also* gives $|P_x|$ in agreement with experiment. Hence if the integrals were halved we could in this case only say that the orbitals were polar, but the intensity argument would no longer predict the direction of the polarity. We consider, however, an α of 0.9999 to be unreasonable, so the conclusion that the MO's are polarized toward the H remains more plausible.

N.m.r. and Exchange Equivalence of the Hydrogens in ReH$_9^{-2}$.—High resolution proton resonance spectra of solutions of K_2ReH_9 show only a single line[5,7] indicating that all the hydrogens are closely equivalent in regard to their electronic environment. The hydrogens have also been found to be equivalent in their rate of exchange with alkaline[7] D$_2$O. These results are made understandable by the fact that all the Re–H distances are nearly the same and that the hydrogen environment of both prism (H atoms 1–6 in Fig. 3) and equatorial hydrogens (7–9, Fig. 3) is quite similar. Thus, in the idealized model used for the MO calculation, an equatorial H (*e.g.*, 9) has four nearest neighbors (1, 3, 4, 6) distant 1.90 Å., while a prism H (*e.g.*, 1) also has four neighbors (2, 3, 7, 9) at about the same distance: two H (7 and 9) at 1.90 Å. and two H (2 and 3) at 2.04 Å. Furthermore, there exist deformation modes which, if they take place with sufficient amplitude, interchange the prism and equatorial hydrogens. One component of a symmetry mode (species

E') which has this property is illustrated in Fig. 6. For the prism and equatorial hydrogens to interchange their positions, H_1, H_4, H_7, and H_9 must undergo a motion of 0.44 Å. while H_2, H_3, H_5, and H_6 must be displaced 0.23 Å. Such displacements do not take place in the solid despite amplitudes of thermal motion comparable with those required for interchange (*cf.*, Table VII). The absence of interchange between prism and equatorial hydrogen atoms in the crystal leads to the inference of a large potential barrier to the deformation modes required for such a transformation. However, for the unconstrained ReH_9^{-2} ion in solution, the required displacements are quite reasonable and may be expected to take place, so that all nine H appear equivalent in the n.m.r. and exchange experiments. A similar explanation has been given for the n.m.r. equivalence of the fluorines in PF_5.[29]

(29) R. S. Berry, *Rev. Mod. Phys.*, **32**, 447 (1960).

Transition Metal–Hydrogen Compounds. III. Dipotassium Enneahydridotechnate(VII)

BY A. P. GINSBERG

Reduction of ammonium pertechnate with potassium metal in ethylenediamine–ethanol medium yields K_2TcH_9. Powder patterns show this compound to be isostructural with K_2ReH_9. The lattice constants of the hexagonal unit cell are $a = 9.64$ and $c = 5.56$ Å. The high resolution proton n.m.r. spectrum of a solution of K_2TcH_9 has a broad line at τ 18.4 p.p.m. This is attributed to the metal-bonded hydrogens. The infrared spectrum of solid K_2TcH_9, like that of K_2ReH_9, shows a triplet in the M–N stretching region and a singlet in the M–N bending region. The chemical behavior of the technetium and rhenium hydrides is similar, but the technetium compound is more reactive.

The existence of a water-soluble potassium rhenium hydride[1,2] having the composition K_2ReH_9[3] suggested a search for similar complexes of other transition metals. An obvious possibility is technetium, which in most of its chemical properties is like rhenium. Indeed, tracer experiments[4] have shown that under conditions where rhenium forms a hydride, technetium yields a compound with apparently similar solubility characteristics and similar behavior toward acid. The present paper describes the preparation, characterization, and some properties of the technetium analog of K_2ReH_9.

Experimental

Preparation.—NH_4TcO_4 (50–100 mg., spectroscopically pure, prepared *via* the heptoxide from metallic Tc^{99} obtained from the Oak Ridge National Laboratory) was dissolved in 100 ml. of 4:1 anhydrous ethylenediamine–absolute ethanol containing 2% C_2H_5OK. Under a nitrogen atmosphere, and with vigorous stirring, 5 g. of clean potassium metal was added at such a rate that the temperature rise was just sufficient to melt the metal. The light brown solid which formed was washed, successively, with the reaction solvent, anhydrous ethylenediamine, 1,2-dimethoxyethane, and ether. Exclusion of moisture is essential during the above operations, and the dimethoxyethane and

ether should be freshly distilled from $LiAlH_4$. Microscopic examination of the product shows it to consist of a white solid admixed with small amounts of a brown solid, presumably metallic technetium or a lower oxide. Infrared spectra indicate the presence of small amounts of carbonate, pertechnate, and ethylenediamine. Because of the presence of these impurities, and the great sensitivity of the product to moisture, an attempt to establish the composition by analysis has not been made. However, as will be seen below, the results of several chemical and physical studies demonstrate conclusively the hydridic nature of the product and the fact that the hydrogens are directly bonded to the technetium. Furthermore, comparison with the corresponding results for K_2ReH_9, especially the X-ray diffraction patterns and infrared spectra, make it quite certain that the technetium and rhenium compounds have the same stoichiometry and structure.

Chemical Properties.—On adding the solid to water hydrogen is evolved and a brown-black precipitate forms. With dilute acids the hydrogen evolution is very vigorous, and the precipitate (Tc metal or a lower oxide) is black and so finely divided that an identifiable X-ray diffraction pattern could not be obtained. Small quantities of the hydride are soluble in strong aqueous alkali (20–50% KOH) with only slight decomposition, and the resulting solutions appear to be unchanged on standing overnight, as shown by their reduction of $TlNO_3$ to the metal and their behavior on acidification. However, alkaline solutions containing > ~0.05% of the hydride decompose rapidly at room temperature. With alkaline NaOCl there is vigorous evolution of hydrogen and the technetium is oxidized to TcO_4^-. The behavior of K_2ReH_9 is quite similar.[1,2] Noteworthy differences are that even relatively concentrated solutions of K_2ReH_9 in strong aqueous alkali are stable at room temperature, and that with $TlNO_3$ the rhenium compound gives an intermediate white solid (pre-

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