

Trimagnesium rhenium(I) heptahydride, Mg_3ReH_7 , containing octahedral $[\text{ReH}_6]^{5-}$ complex anions

B. Huang and K. Yvon*

Laboratoire de Cristallographie, Université de Genève, 24, quai E. Ansermet, CH-1211 Genève (Switzerland)

P. Fischer

Laboratorium für Neutronenstreuung, Eidgenössische Technische Hochschule Zürich & Paul Scherrer Institut, CH-5232 Villigen PSI (Switzerland)

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Abstract

Mg_3ReH_7 and its deuteride were synthesized by the reaction of magnesium and rhenium powders at 510–520 °C and 120–155 bar hydrogen (deuterium) pressure and characterized by X-ray and neutron powder diffraction. They crystallize with hexagonal symmetry (space group $P6_3/mmc$ (No. 194); hydride: $a = 4.8615(2)$ Å, $c = 10.5937(5)$ Å; deuteride: $a = 4.8539(2)$ Å, $c = 10.5699(7)$ Å). The structure contains a nearly regular octahedral 18-electron $[\text{ReD}_6]^{5-}$ complex anion with bond distances $[\text{Re}-6\text{D}1] = 1.724(4)$ Å and a D^- anion coordinated by five magnesium atoms in a trigonal bipyramidal configuration with bond distances $[\text{D}2-2\text{Mg}1] = 1.901(4)$ Å and $[\text{D}2-3\text{Mg}2] = 2.8024(1)$ Å.

1. Introduction

The only ternary complex rhenium hydride known is K_2ReH_9 . It was synthesized by the reaction of KReO_4 with K metal in an ethylenediamine–water solution and found to contain tricapped trigonal prismatic 18-electron $[\text{ReH}_9]^{2-}$ anions [1]. In this paper we report another rhenium-based complex ternary metal hydride, Mg_3ReH_7 . It was synthesized by a solid state reaction under hydrogen pressure and found to contain a mixture of an octahedral $[\text{ReH}_6]^{5-}$ complex anion conforming to the 18-electron rule and an H^- anion.

2. Experimental details

2.1. Synthesis

Mixtures of magnesium powder (CERAC, 400 mesh, 99.6%) and rhenium powder (Johnson–Matthey, Specpure) in the atomic ratio $\text{Mg}:\text{Re} = 3.15:1$ were pressed into pellets and placed in a high temperature, high pressure autoclave. After evacuating to about 10^{-5} bar and flushing several times with argon, the autoclave was charged with hydrogen (deuterium) gas (Polygaz, Genève, 99.9999% for H_2 ; AGA, 99.8% for D_2) to an initial pressure of about 75 bar at room temperature.

The temperature was increased to 510–520 °C, yielding a hydrogen (deuterium) pressure of 155 bar, held at that level for 2 weeks, during which the pressure decreased to about 120 bar, and then lowered to ambient temperature. After releasing the hydrogen (deuterium) pressure, the autoclave was opened and the samples transferred to an argon-filled glove-box. The final products had a grey colour and were sensitive to air.

2.2. X-Ray and neutron diffraction

The samples were characterized by X-ray powder diffraction at room temperature (Guinier camera with sealed capillaries and Guinier diffractometer [2], $\text{Cu K}\alpha_1$ radiation; internal standard: silicon powder, $a = 5.4308$ Å). The films were measured on a computer-controlled microdensitometer [3]. The patterns revealed the presence of a new ternary hydride phase and a small quantity of unreacted rhenium metal. After subtraction of the rhenium peaks, the patterns were indexed on a hexagonal lattice with refined cell parameters $a = 4.8615(2)$ Å, $c = 10.5937(5)$ Å (hydride) and $a = 4.8539(2)$ Å, $c = 10.5699(7)$ Å (deuteride). The reflection intensities were consistent with a metal atom arrangement of composition Mg_3Re as described in space group $P6_3/mmc$ (No. 194) with magnesium in positions $4(f)$: $\frac{1}{3}, \frac{2}{3}, \sim 0.07$, etc. and $2(b)$: $0, 0, \frac{1}{2}$, etc. and rhenium in $2(a)$: $0, 0, 0$, etc. The model (including elemental rhenium) was refined from the diffractometer

*Author to whom correspondence should be addressed.

data by the program DBWS-9006 [4] and converged at the residuals $R_B = 3.6\%$, $R_p = 8.2\%$ and $R_{wp} = 13.5\%$.

The atomic parameters of hydrogen were established by neutron diffraction on the deuteride by using the DMC powder diffractometer [5] at the reactor SAPHIR at PSI, Villigen (Ge(311); $\lambda = 1.7037 \text{ \AA}$, angular 2θ range $3.0\text{--}135.0^\circ$, 2θ step 0.1° , $T = 295 \text{ K}$). The sample (about 3.6 g) was enclosed in a cylindrical vanadium container of 8 mm inner diameter and measured in the high intensity mode. The profile refinements (program DBWS-9006) showed two symmetry-independent deuterium sites: D1 (site 12k) surrounding rhenium in an octahedral configuration and D2 (site 2c) situated in a trigonal bipyramidal hole formed by five magnesium atoms. The impurity phases MgO (not detected by X-rays) and rhenium were included in the refinements. The nuclear scattering lengths (10^{-12} cm) of 0.6671 (D), 0.5803 (O), 0.5375 (Mg) and 0.92 (Re) were taken from ref. 6. Preliminary refinements showed that the occupancy factors of the two deuterium sites did not differ significantly from 100%. Thus they were fixed at unity in the final refinement. Results are summarized in Table 1. Interatomic distances and bond angles are given in Table 2. The observed, calculated and difference neutron patterns are shown in Fig. 1.

3. Results and discussion

The structure of Mg_3ReD_7 can be regarded as an arrangement of deformed cubes of magnesium cations which are centred by octahedral $[ReD_6]^{5-}$ complex anions (Fig. 2). The magnesium cubes are linked via edges to sheets parallel to the hexagonal plane and via corners to a three-dimensional network, similar to the arrangement in $SrMg_2FeD_8$ [7]. In contrast with $SrMg_2FeD_8$, however, in which the sheets all have the same orientation with respect to the trigonal axis and thereby form tetrahedral alkaline earth holes occupied

TABLE 1. Refinement results on neutron powder diffraction data for Mg_3ReD_7 ($T = 295 \text{ K}$)

Atom	Position	x	y	z	U_{iso} (10^{-2} \AA^2)
Mg1	4(f)	$\frac{1}{2}$	$\frac{2}{3}$	0.0702(4)	1.69(6)
Mg2	2(b)	0	0	$\frac{1}{2}$	$U_{iso}(\text{Mg1})$
Re	2(a)	0	0	0	0.07(5)
D1	12(k)	0.1656(5)	2x	0.5962(2)	3.02(4)
D2	2(c)	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{2}$	$U_{iso}(\text{D1})$
Space group	$P6_3/mmc$ (No. 194)				
Cell parameters	$a = 4.8539(2)$, $c = 10.5699(7) \text{ \AA}$				
Agreement indices	$R_B = 5.4\%$, $R_F = 4.6\%$, $R_p = 2.9\%$, $R_{wp} = 3.9\%$				
Form of temperature factor	$T = \exp[-8\pi^2 U_{iso}(\sin \theta/\lambda)^2]$				

Estimated standard deviations in parentheses.

TABLE 2. Interatomic distances (\AA) up to 3.5 \AA , D–D contact distance (\AA), and R–Re–D bond angles ($^\circ$) for Mg_3ReD_7 ($T = 295 \text{ K}$) (from neutron data)

Re–6D1	1.724(4)	D1–Re	1.724(4)
2Mg2	2.6425(2)	Mg2	2.140(2)
6Mg1	2.899(1)	Mg1	2.254(5)
Mg1–D2	1.901(4)	2Mg1	2.443(5)
3D1	2.254(5)	2D1	2.411(4)
6D1	2.443(5)	D2–2Mg1	1.901(4)
3Re	2.899(1)	3Mg2	2.8024(1)
3Mg1	3.171(3)	D1–Re–2D1	91.2(2)
3Mg2	3.386(2)	D1–Re–2D1	88.8(2)
Mg2–6D1	2.140(4)		
3D2	2.8024(1)		
2Re	2.6425(2)		
6Mg1	3.386(2)		

Estimated standard deviations in parentheses.

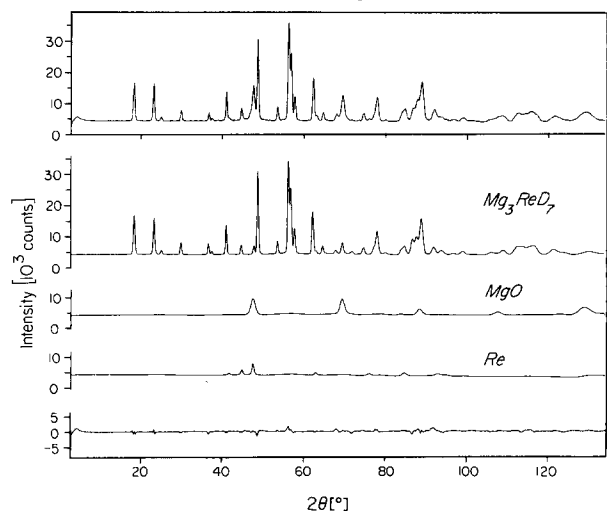


Fig. 1. Observed (top), calculated (middle) and difference (bottom) neutron diffraction patterns of Mg_3ReD_7 , with impurity phases MgO and Re ($\lambda = 1.7037 \text{ \AA}$).

by deuterium, the sheets in Mg_3ReD_7 are rotated alternately by 60° or -60° about the hexagonal axis, thereby leaving trigonal bipyramidal magnesium holes occupied by deuterium. The structural features are consistent with the assumption of an 18-electron transition metal complex and deuteride anions as indicated by the limiting ionic formula $3Mg^{2+}[ReD_6]^{5-}D^-$. The octahedral complex is almost regular (bond angles D–Re–D = $88.8(2)^\circ$ – $91.2(2)^\circ$) and its bond distances $[Re-6D1] = 1.724(4) \text{ \AA}$ are slightly longer than the average bond distance $[Re-H]_{av} = 1.68 \text{ \AA}$ in the two tricapped trigonal prismatic $[ReH_9]^{2-}$ complexes in K_2ReH_9 [1]. The bond distances between magnesium and deuterium (D1) in the complex, $[Mg-D] = 2.14\text{--}2.44 \text{ \AA}$, are consistent with the corresponding distances in ternary Mg_2FeD_6 ($[Mg-D] = 2.22 \text{ \AA}$ [8]) and quaternary $SrMg_2FeD_8$ ($[Mg-D] = 2.21\text{--}2.26 \text{ \AA}$ [7]). Those involving

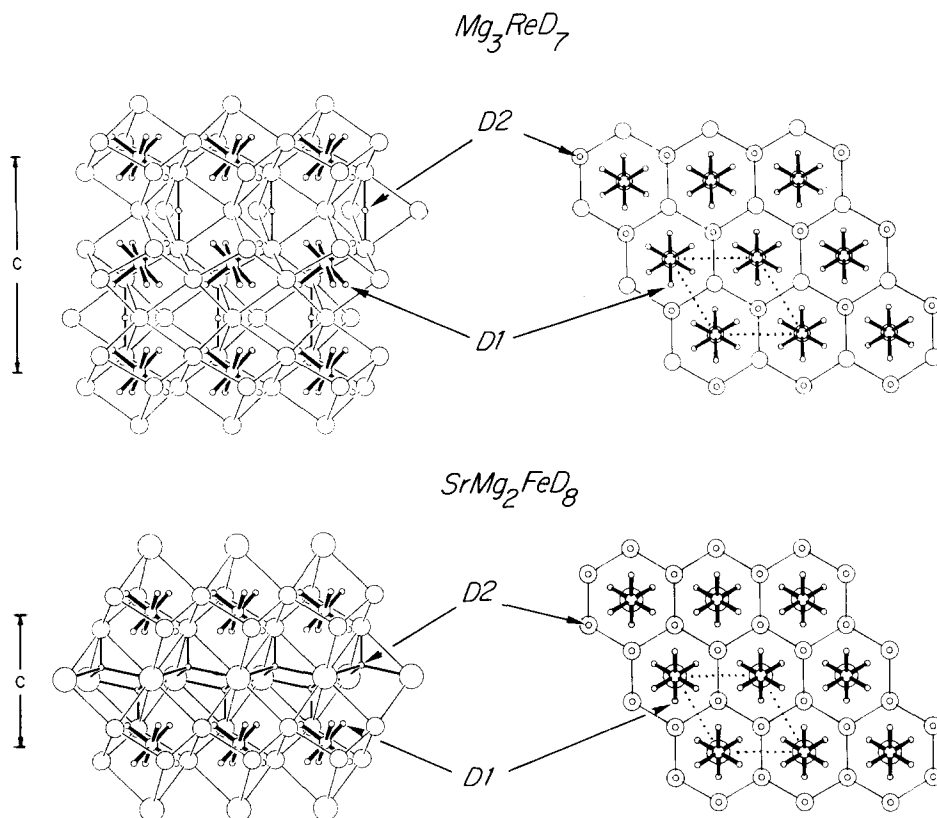


Fig. 2. Structure of hexagonal Mg_3ReD_7 , as compared with trigonal $SrMg_2FeD_8$ perpendicular (left) and parallel (right) to the hexagonal (or trigonal) axis.

the quasi-linear coordinated deuterium (D2) in the trigonal bipyramidal hole, $[Mg-D] = 1.90 \text{ \AA}$, are shorter than those in binary MgD_2 ($[Mg-D] = 1.95 \text{ \AA}$).

The octahedral hydride complex $[Re(I)D_6]^{5-}$ is the first such complex known for rhenium. Examples of octahedral hydride complexes containing other transition elements with higher formal oxidation states are $[TD_6]^{4-}$, $T \equiv Fe(II)$ [8], $Ru(II)$ [9] and $Os(II)$ [10], and $[TD_6]^{3-}$, $T \equiv Rh(III)$ and $Ir(III)$ [11]. All these complexes conform to the 18-electron rule and contain transition elements which have presumably a d^6 low spin configuration.

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