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Letter

Structure of $KNaReH_9$ by single crystal X-ray diffraction and infrared spectroscopy

N.T. Stetson, K. Yvon

Laboratoire de Cristallographie, Université de Genève, 24, quai-Ernest-Ansermet, CH-1211 Genève 4, Switzerland

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Abstract

Single crystals of $KNaReH_9$ were grown from a 0.3 M solution of Na_2ReH_9 in 3 M KOH. The solution and refinement of the single crystal X-ray diffraction data (space group *Pnma:* $a=9.2045(9)$; $b=5.4218(5)$; $c=10.1195(10)$; $R=0.042$) show that the metal atoms adopt the TiNiSi-type structure. No hydrogen atom locations were found in the different electron density maps. The alkali metal atoms form tricapped trigonal prisms around the Re sites, forming a similar environment to that found in K_2ReH_9. The measured IR spectra are consistent with those reported for other tricapped trigonal prismatic $[ReH_9]^{2-}$ complexes. The calculated hydrogen density is 117 g H l^{-1}.

Keywords: Single crystal X-ray diffraction; Infrared spectroscopy

1. Introduction

Of the reported nonahydridorhenate salts, structural determinations had, until recently, only been published for dipotassium nonahydridorhenate, K_2ReH_9 [1]. These compounds are of interest because of the uniqueness of the nonahydridorhenate anion $[ReH_9]^{2-}$. This anionic complex contains the highest number of hydrogen per metal (9:1) and the rhenium has the highest formal oxidation state (VII) found in metal hydride complexes. We have therefore undertaken an investigation into the other salts of this series in order to further understand this complex. This work led to the recent publication of the $BaReH_9$ structure [2] and here we present the $KNaReH_9$ metal atom structure.

2. Experimental

Disodium nonahydridorhenate was prepared according to published procedures [3]. Crystals of $KNaReH_9$ were grown by slow evaporation under flowing argon of a 0.3 M solution of Na_2ReH_9 in 3 M KOH. Over a period of about 3 weeks, large (up to several millimetres in diameter) translucent crystals were formed. An irregularly shaped piece broken from one crystal was coated with a 2.5/1 mixture of RS3000/Hostinert 216 perfluorpolyethers and mounted on a glass fibre under a cold nitrogen stream [4].

An X-ray diffraction data collection was performed on an Enraf-Nonius CAD4 diffractometer using Cu Kα radiation with a graphite monochromator. The crystal was kept in a cold nitrogen stream at approximately 193 K. The data reduction, solution and refinement were performed using programs in the Xtal3.2 program package [5]. The orthorhombic lattice parameters ($a=9.2045(9)$, $b=5.4218(5)$, $c=10.1195$ (10) Å; $V=505.0$ (1) Å^3) were refined using 2θ angles of 25 reflections ($20\leqslant 2\theta\leqslant 90$). The full diffraction sphere between 4° and 120° 2θ ($-10\leqslant h\leqslant 10$; $-6\leqslant k\leqslant 6$; $-11\leqslant l\leqslant 11$) was measured using the ω-2θ scan mode, giving 3317 reflections, 476 unique reflections ($R_{equiv.}=9.7\%$). Two standard reflections, 2 1 1 and -3 2 2, showed intensity variations of 1.4%. The systematic extinctions corresponded to either space group $Pn2_1a$ or *Pnma*, the centrosymmetric space group, *Pnma* (No. 62), was chosen for the structure solution. A spherical absorption correction, mean radius equal to 0.032 mm, was made using LSABS [6] with minimum and maximum transmission factors of 0.1000 and 0.1981. The Re and K positions were found by direct methods with MULTAN87 [7] and the Na position from difference

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Table 1
Atomic positional and anisotropic thermal displacement parameters

Atom	Site	x	y	z
Re	4c	0.2698(1)	1/4	0.3832(1)
Na	4c	0.1370(1)	1/4	0.075(1)
K	4c	0.0290(7)	1/4	0.6748(6)
Proposed H positions, not refined				
H1	8d	0.410	0.050	0.414
H2	8d	0.230	0.050	0.260
H3	8d	0.180	0.050	0.485
H4	4c	0.395	1/4	0.260
H5	4c	0.348	1/4	0.535
H6	4c	0.086	1/4	0.357

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K	0.014(3)	0.008(3)	0.021(3)	0	0.002(3)	0
Na	0.012(5)	0.013(6)	0.022(6)	0	−0.001(5)	0
Re	0.0040(7)	−0.0004(7)	0.0117(7)	0	0.0002(5)	0

Table 2
Selected interatomic distances (Å)

Re– 1×Na	3.348(11)	Na– 1×Re	3.348(11)
1×Na	3.402(11)	1×Re	3.402(11)
2×Na	3.446(7)	2×Re	3.446(7)
1×K	3.688(6)	2×Na*	3.999(11)
2×K	3.903(4)	2×K*	4.010(9)
2×K	3.906(4)		
2×Re*	5.334(2)		
K– 1×Re	3.688(6)		
2×Re	3.903(4)		
2×Re	3.906(4)		
2×Na*	4.010(9)		
2×K*	4.485(7)		

* For the Re–Re and alkali–alkali distances, only the shortest contacts are given.

electron density maps. The population parameters were found not to vary significantly from unity, and were therefore fixed at full occupancy for the final refinements. A refinement using |F| values of 418 unique, observed reflections, converged to $R=0.042$ (unit weights). A secondary extinction correction was refined to $G=0.13$ (1). The max. shift/e.s.d. in the last cycle was 0.0003. The final residual electron density was +2.96 (−1.80) e^- $Å^{-3}$. No hydrogen atom locations were found in the difference electron density maps. Atomic coordinates were standardized with STRUCTURE TIDY [8]. Atomic positional and thermal displacement parameters are given in Table 1. Selected interatomic distances are shown in Table 2.

The IR spectrum of ground crystals was measured in KBr pellets on a Perkin-Elmer 880 spectrophotometer. Table 3 gives a comparison of the IR spectra to those reported for other $[ReH_9]^{2-}$ salts.

Table 3
A comparison of the IR spectra reported for various $[ReH_9]^{2-}$ salts

Compound	Frequency (cm^{-1})	Assignment	Ref.
$KNaReH_9$	738 s (745)		[3]
	~1700 sh (~1750)		(this work)
	1845 s (1854)		
	~1950 sh (~1950)		
K_2ReH_9	~670 sh		[12]
	730(8)	e', a″$_2$	
	~1710 sh	a″$_2$	
	1840(10) br	a″$_2$	
	1925(1)	a′$_2$	
$BaReH_9$	~640 sh		[2]
	690 s		
	~740 sh		
	~1830 sh		
	1870 s, br		
	~2000 sh		
Na_2ReH_9	~630 sh		[3]
	~720 sh		
	745 s	e′ or a″$_2$	[13]
	1835 s, br		

s, strong; br, broad; sh, shoulder.

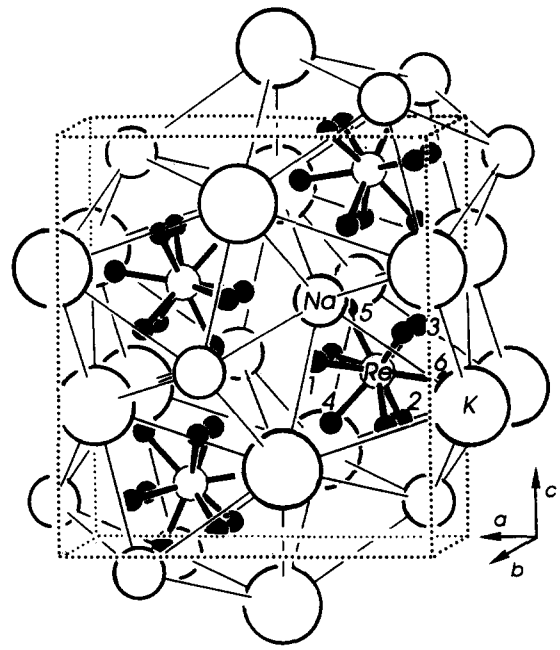

Fig. 1. Metal atom structure of $KNaReH_9$. The alkali atoms have been connected to emphasize the tricapped trigonal prisms. One unit cell is shown. Large circles, K; medium circles, Na; small circles, Re; small, filled circles, H.

3. Results and discussion

$KNaReH_9$ can be formed from either the disodium or dipotassium salts, indicating that it is a unique salt with a lower solubility than either the pure disodium or dipotassium salts [3]. This observation is born out by the structure data. The K and Na atoms occupy

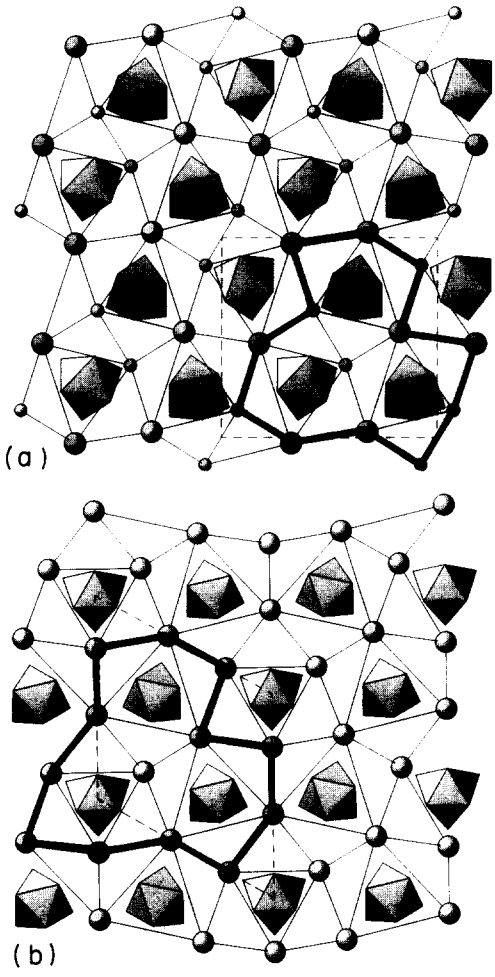

Fig. 2. Comparison of (a) orthorhombic $KNaReH_9$ (0 1 0 projection) and (b) hexagonal K_2ReH_9 (0 0 1 projection) structures. The $[ReH_9]^{2-}$ anions are represented as polyhedra. Highlighted regions show isostructural units; one unit cell is shown for each.

distinct crystallographic sites with no apparent mixing. The metal atom substructure, shown in Fig. 1, is isostructural to the TiNiSi type structure [9]. The Re environment is very similar to that found in the K_2ReH_9 structure. In both, the Re centers a tricapped trigonal prism of alkali metal atoms. In the $KNaReH_9$ structure, the trigonal prisms are composed of 4 K and 2 Na atoms and 2 Na and 1 K atoms form the caps. The mixture of the two alkali metal distort the tricapped trigonal prisms with shorter Re–Na distances than Re–K. The distances range from 3.35–3.44 Å and 3.69–3.91 Å for the Na and K respectively (see Table 3); in the dipotassium salt, the Re–K distances range from 3.62–4.00 Å [1(a)]. Fig. 2 shows a comparison of the two structures. As can be seen by the highlighted areas, similar structural units composed of three of the alkali metal tricapped trigonal prisms can be found in the two structures. The differences in the structures become apparent in the way these isostructural units are connected together. Also the K_2ReH_9 metal atom structure is that of the Fe_2P type [10]; a comparison of the TiNiSi and Fe_2P types has been given previously [11]. A nearly regular tricapped trigonal prism of hydrogen around the Re can be formed by placing hydrogen atoms on three 8*d* (*x*,*y*,*z*) sites and three 4*c* (*x*,1/4,*z*) sites, as given in Table 1. The calculated hydrogen density of this compound is 117 g H l^{-1}.

The measured IR spectrum compares well with those reported for the other $[ReH_9]^{2-}$ salts. Table 3 shows the comparison along with the assignments which have been made for the various stretching modes.

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References

[1] (a) K. Knox and A.P. Ginsberg, *Inorg. Chem., 3* (1964) 555; (b) S.C. Abrahams, A.P. Ginsberg and K. Knox, *Inorg. Chem., 3* (1964) 558.

[2] N.T. Stetson, K. Yvon and F. Fischer, *Inorg. Chem., 33* (1994) 4598.

[3] (a) A.P. Ginsberg and C.R. Sprinkle, *Inorg. Chem., 8* (1969) 2212; (b) A.P. Ginsberg and C.R. Sprinkle, *Inorg. Synth., 13* (1972) 219.

[4] T. Kottke and D. Stalke, *J. Appl. Crystallogr., 26* (1993) 615.

[5] S.R. Hall, H.D. Flack and J.M. Stewart (eds.), *Xtal3.2 Reference Manual,* University of Western Australia, Perth, 1992 (and references therein).

[6] E. Blanc, D. Schwarzenbach and H.D. Flack, *J. Appl. Crystallogr., 24* (1991) 1035.

[7] T. Debaerdemaeker, G. Germain, P. Main, C. Tate and M.M. Woolfson, MULTAN87, *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data,* University of York.

[8] L.M. Gelato and E. Parthé, *J. Appl. Crystallogr., 20* (1987) 139.

[9] C.B. Shoemaker and D.P. Shoemaker, *Acta Crystallogr., 18* (1965) 900.

[10] E. Parthé, L.M. Gelato, B. Chabot, M. Penzo, K. Cenzual and R.E. Gladyshevskii, TYPIX, *Standardized Data and Crystal Chemical Characterizations of Inorganic Structure Types in Gmelin Handbook of Inorganic and Organometallic Chemistry,* 8th edn., Springer, Berlin, 1993.

[11] W.X. Zhong, B. Chevalier, J. Etourneau and P. Hagenmuller, *Mater. Res. Bull., 22* (1987) 331.

[12] J.A. Creighton and T.J. Sinclair, *J. Chem. Soc., Faraday Trans., 270* (1974) 548.

[13] J.W. White and C.J. Wright, *J. Chem. Soc., Faraday Trans., 68* (1972) 1414.