JOURNAL OF SOLID STATE CHEMISTRY 92, 514–519 (1991)

Preparation and Structure of the Ternary Hydrides Li_4RuH_6, Na_4RuH_6, and Li_4OsH_6 Containing Octahedral Transition Metal Hydrogen Complexes

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Received October 3, 1990; in revised form February 18, 1991

Li_4RuH_6, Na_4RuH_6, and Li_4OsH_6 have been synthesized. Structure determinations based on X-ray and neutron powder diffraction data revealed the hydrides to have the rhombohedral K_4CdCl_6 type structure in space group $R\bar{3}c$ (167). With a hexagonal setting the triple unit cell dimensions were Li_4RuH_6: $a = 8.1686(29)$ Å, $c = 10.0255(15)$ Å; Na_4RuH_6: $a = 9.1526(6)$ Å, $c = 11.3778(11)$ Å; Li_4OsH_6: $a = 8.2468(38)$ Å, $c = 10.1187(36)$ Å, and $Z = 6$. The structure can be characterized by isolated MH_6^{4-} (M = Ru, Os) ions located in a cube of alkali metal ions. The low formal oxidation state of the transition metal atom was attributed to the large polarizability of the metal–hydrogen bond.

Introduction

A number of ruthenium-based ternary hydrides with the K_2PtCl_6 type structure have been synthesized to date, where an octahedral $[RuH_6]^{4-}$ complex is counterbalanced by divalent electropositive alkaline earth or rare earth metal ions (*1*). This would give ruthenium a formal oxidation state of +II, and the stability of the complex is explained by referring to electronic factors in the form of the 18 electron rule. The structure can be described as being built up by cubes of the electropositive metal ions, with every second cube containing an octahedral complex in the center with the hydrogen ligands pointing toward the face centers. More recently this type of structure has also been found with octahedral iron and osmium complexes in Mg_2FeH_6 and Mg_2OsH_6 (*2, 3*). Usually a low formal oxidation state of a transition metal complex is associated with an electron accepting ligand that has empty

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0022-4596/91 $3.00

π^* or d orbitals available to accept the high electron density of the central metal atom. This stabilization grows in importance when going from the first to the third row of the transition metals, and it is somewhat surprising to find a formally divalent osmium complex with hydrogen as the only ligand, since osmium(II) complexes are known to be stable only with ligands having good electron acceptor properties.

To investigate the counterion influence and also the possibilities to obtain other oxidation states, we tried to synthesize related ternary hydrides based on iron, ruthenium, and osmium complexes, with alkali metal counterions. This led to the discovery of three new hydrides: Li_4RuH_6, Na_4RuH_6, and Li_4OsH_6, the synthesis, structure, and properties of which are the object of the present paper.

Experimental

The hydrides were made by sintering the alkali hydrides LiH, NaH, and KH with iron, ruthenium, and osmium metal powders in hydrogen. The starting materials were delivered by Aldrich from their standard assortment. The reaction route to the new hydrides was optimized in a screening test where the temperature, the hydrogen pressure, and the alkali hydride to transition metal ratio were varied. The reaction products from each sample, which had a weight of a few tenths of a gram, were investigated by Guinier–Hägg X-ray diffraction to characterize the samples with respect to their crystalline components. To facilitate the reaction, the alkali hydride and the metal powder were mixed and pressed into tablets before the heating in hydrogen. Standard Alsint reaction tubes were used to contain the samples during the reactions, which were performed in a stainless steel autoclave inserted in a tube furnace. An iron–constantan thermocouple, encapsulated in a stainless steel capillary contacted to the sample, monitored any evolved reaction heat. The relative poor heat conductivity of the hydrides made this a sensitive method to observe the onset and the initial faster part of the reaction. The synthesis could also be followed by measuring the hydrogen consumption. This was done by observing the pressure drop in a small calibrated volume before the reducing valve that admits the hydrogen into the reaction chamber, but as the accuracy is very dependent on sample size, this could only be used with confidence in the final synthesis, where we were working with sample sizes of a few grams to determine the composition of the hydrides.

The general findings were that iron could not be made to react with any of the three alkali hydrides at temperatures below 800°C at a maximum pressure of 100 bar, which were the structural limitations imposed on our set up. Lithium hydride could be made to react both with ruthenium and osmium. Sodium hydride did react with ruthenium but not with osmium, and potassium hydride did not react with any of the three transition metals. The optimum reaction temperature was found to be around 480°C; above 500°C the samples tended to decompose and at lower temperatures the reaction time became too long. The reaction rate was also influenced by the hydrogen pressure in that an increased pressure did speed up the reaction, but already with a hydrogen pressure of 10 bars at 480°C most of the reaction was completed within a few hours. To ensure that the samples would be as homogeneous as possible the reactions were, however, allowed to proceed for several days. The new hydrides deteriorated quickly in air, and the samples were therefore always handled under continuously purified argon. In the samples that reacted a new set of diffraction lines appeared in the X-ray diffraction records. From the samples with lithium hydride and ruthenium or osmium we found that with body-centered cubic unit cells of

TABLE I

UNIT CELL DIMENSIONS OF K_4CdCl_6 TYPE TERNARY HYDRIDES DETERMINED FROM GUINIER–HÄGG X-RAY DATA USING SILICON AS INTERNAL STANDARD AND Cu$K\alpha_1$ RADIATION (λ = 1.5405981 Å) AND THEIR CALCULATED X-RAY DENSITIES

Li_4RuH_6	Na_4RuH_6	Li_4OsH_6
a = 8.1686(29)	a = 9.1526(6)	a = 8.2468(38)
c = 10.0255(15)	c = 11.3778(11)	c = 10.1187(36)
V = 579.34 Å^3	V = 825.44 Å^3	V = 595.99 Å^3
M_{15} = 48	M_{36} = 51	M_9 = 75
D_c = 2.329 g · cm^{-3}	D_c = 2.412 g · cm^{-3}	D_c = 3.759 g · cm^{-3}
Li_4RuD_6	Na_4RuD_6	Li_4OsD_6
a = 8.1663(14)	a = 9.1449(3)	a = 8.2308(36)
c = 9.9761(20)	c = 11.3560(2)	c = 10.0944(51)
V = 576.16 Å^3	V = 822.46 Å^3	V = 592.58 Å^3

dimensions a = 5.76 Å and a = 5.83 Å, respectively, the new diffraction lines could be indexed. The diffraction lines from the sodium ruthenium hydride showed, however, deviations from the cubic symmetry, but from the similarities of the diffraction patterns we concluded that all three new hydrides were isotypic, having a pseudocubic structure.

By varying the alkali hydride to transition metal ratio in the syntheses we determined the composition of the new hydrides to be Li_4OsH_6, Li_4RuH_6, and Na_4RuH_6, respectively. This suggested the rhombohedral pseudocubic K_4CdCl_6 type structure for these new hydrides (*4*). The refined hexagonal triple cell dimensions are given in Table I, with their calculated X-ray densities. All X-ray photographs were taken in a subtraction-geometry Guinier-Hägg focusing camera, with monochromatic Cu$K\alpha_1$ radiation (λ = 1.5405981 Å). Single-coated film (CEA Reflex 15) was used through all the work. The films were evaluated by means of a computer-controlled single-beam microdensitometer designed for X-ray powder photographs (*5*). The θ scale was calibrated by the internal standard technique using a parabolic correction curve. Silicon (a = 5.430880(35) Å at 25°C) was used as standard substance.

The structure was further confirmed by a Rietveld refinement of Na_4RuH_6 based on the X-ray powder pattern (*6*). The resulting position parameters for the metal atoms were, within a few standard deviations, the same as for the K_4CdCl_6 structure. As hydrogen is a very weak X-ray scatterer, the hydrogen positions were determined from the corresponding deuterides, by neutron diffraction. The deuterides were synthesized in conformity with the hydrides. With our rather crude set-up we could not observe any differences in reactivity between the isotopical species. The ruthenium-based deuterides were measured on the "DMC" multicounter powder diffractometer (*7*) at the reactor Saphir in Würenlingen, Switzerland, with an incident neutron wavelength of 1.090 Å. Li_4OsD_6 was measured in Studsvik, Sweden with a neutron wavelength of 1.470 Å. The results from the structural refinements using the DBW3.2S program are given in Table II(*6*).

Since lithium has a fairly high neutron absorption cross section, we had to limit the thickness of the sample to a thin-walled aluminum tube with an inner diameter of 5 mm to get optimum scattered intensity. The same sample holder had to be used for Na_4RuD_6 also, as we had only a limited amount of sample available due to difficulties in synthesizing NaD. This is the main reason for the higher R-values reported in Table II, but traces of unreacted NaD and Ru were also revealed in the diffraction pattern. The amounts were too small to allow a separate refinement of these phases, however.

Discussion

The new hydrides resemble the alkaline earth–transition metal hydrides mentioned

TABLE II

POSITIONAL PARAMETERS, ISOTROPIC TEMPERATURE FACTORS AND INTERATOMIC DISTANCES OF THE TERNARY HYDRIDES A_4RuD_6 (A = Li,Na) AND OF Li_4OsD_6 IN SPACE GROUP $R\bar{3}c$ (167) WITH A HEXAGONAL SETTING, $Z = 6$

Atom	Site	x	y	z	B_{iso}(Å^2)
	Li_4RuD_6, $R_F = 4.38$		$R_{wp} = 6.61$	$\lambda = 1.0901$ Å	
Ru	6(b)	0	0	0	0.6(1)
Li(1)	6(a)	0	0	$\frac{1}{4}$	1.1(1)
Li(2)	18(e)	0.385(2)	0	$\frac{1}{4}$	1.1(1)
D	36(f)	0.187(1)	0.040(1)	0.100(1)	2.1(1)
	Na_4RuD_6, $R_F = 7.97$		$R_{wp} = 9.76$	$\lambda = 1.0901$ Å	
Ru	6(b)	0	0	0	0.6(3)
Na(1)	6(a)	0	0	$\frac{1}{4}$	3.0(4)
Na(2)	18(e)	0.389(2)	0	$\frac{1}{4}$	3.0(4)
D	36(f)	0.176(1)	0.034(1)	0.089(1)	1.7(2)
	Li_4OsD_6, $R_F = 5.38$		$R_{wp} = 8.62$	$\lambda = 1.470$ Å	
Os	6(b)	0	0	0	0.7(2)
Li(1)	6(a)	0	0	$\frac{1}{4}$	1.3(4)
Li(2)	18(e)	0.410(2)	0	$\frac{1}{4}$	1.3(4)
D	36(f)	0.200(1)	0.050(1)	0.085(1)	2.5(2)

Interatomic distances (Å)

Li_4RuD_6	
Ru–D	1.714(5)
Ru–Li(1)	2.494
Ru–Li(2)	2.671(5)
Ru–Ru	4.988
Ru–Ru	4.788
D–Li(1)	2.045(5)
D–Li(2)	2.121(4)
Li(1)–Li(1)	4.988
Li(1)–Li(2)	3.034(4)
Na_4RuD_6	
Ru–D	1.792(9)
Ru–Na(1)	2.839
Ru–Na(2)	2.983(7)
Ru–Ru	5.678
Ru–Ru	6.497
D–Na(1)	2.352(9)
D–Na(2)	2.408(8)
Na(1)–Na(1)	5.678
Na(1)–Na(2)	3.404(6)
Li_4OsD_6	
Os–D	1.712(10)
Os–Li(1)	2.524
Os–Li(2)	2.628(5)
Os–Os	5.047
Os–Os	5.823
D–Li(1)	2.134(9)
D–Li(2)	2.229(11)
Li(1)–Li(1)	5.047
Li(1)–Li(2)	3.005(5)

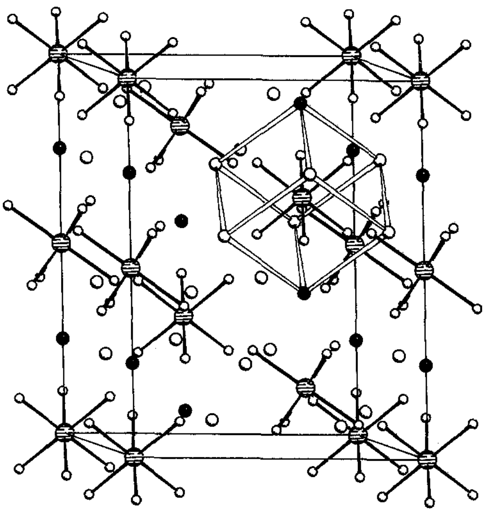

FIG. 1. The structure of the new ternary hydrides with octahedral transition metal–hydrogen complexes in an alkali metal framework. Large circles are transition metal atoms, medium unfilled and filled represent alkali $A(1)$ and $A(2)$ metal atoms, respectively. Small circles are hydrogen atoms. The characteristic alkali metal ion cube surrounding the MH_6^{4-} unit is marked with open lines in this K_6CdCl_6 type structure.

in the introduction: these too consist of octahedral complexes MH_6^{4-} surrounded by cubes of electropositive counterions (cf. Fig. 1). With alkali metal A^+ counterions however, two different A^+ types can be distinguished. $A^+(1)$ links the octahedral MH_6^{4-} groups together to form chains in the c-direction, and $A^+(2)$ is inserted in the spaces between the chains. The $A^+(1)$, located in positions 6(a), has a distorted trigonal prism of hydrogen atoms as nearest neighbors. The cubic alkali ion environment completely separates the anions from each other, which is a common feature of this type of hydride.

The colors of Li_4RuH_6, Li_4OsH_6 (white), and Na_4RuH_6 (green) indicate that these compounds are insulators. Band structure calculations on a similar hydride, Ca_2RuH_6, show a band gap of approximately 2 eV (*8*). The band gap in these new hydrides, judged by interatomic distance considerations, ought not to be far from this value. A formally divalent Ru or Os atom provides 6 electrons from its *d*-shell, while the six hydrogen ligands contribute 12 electrons. This electron count gives 18 electrons in the valence shell, and this is the reason for the stability of the compounds and the 4 : 1 molar ratio of alkali to transition metal.

The ruthenium–hydrogen distance is notably sensitive to the size and thus the stabilizing effect of the counterion. Ru–H is 1.71 Å with lithium as counterion, which is in good agreement with the Ru–H distance 1.69(1) Å in Sr_2RuH_6 (*1*). In Na_4RuH_6 the Ru–H distance is 1.79 Å. The alkali to hydrogen distance is, further, close to the value found in the corresponding binary alkali hydride, indicating the importance of an ionic contribution to bonding between the complexes and the counterions in these new hydrides. This is presumably the reason for our failure to produce the corresponding hydrides with potassium as counterion, since the transition metal–hydrogen bond distance in this case would get too long. Related to this is probably also our failure to produce Na_4OsH_6. Already in Na_4RuH_6 the Ru–H distance is unusually long, indicating a weak bond. Since hydrogen is the only ligand on the transition metal, we should expect further destabilization with the growing importance of back donation when going from the second to the third row transition metals.

In this context, however, the existence of Li_4OsH_6 and Mg_2OsH_6 raises a question of fundamental importance. Formally divalent osmium complexes are known to exist only with ligands having good π-accepting properties, such as CN^-, bipy, phen, phosphines. With halide ligands we have to go all the way to I^- in OsI_2 to find enough electron-accepting ligand *d*-orbitals to stabilize formally divalent osmium. Fluoride, F^-, with a size comparable to that of H^-, is known to occur in the formally tetravalent $[OsF_6]^{2-}$ complex and with higher Os oxidation states, e.g., in $Os(VI)F_6$. Similarly hydrogen is known to stabilize high oxidation states, for example in the well known $[ReH_9]^{2-}$ ion (*9*). An $[Os(II)F_6]^{4-}$ complex has, however, not yet been found, the difference being the filled *p*-orbitals on fluorine that will give it a character of π donor instead of π acceptor. Neither has the aquo complex $[Os(II)(H_2O)_6]^{2+}$ been found, although the corresponding complexes are known for both iron and ruthenium (*10*). This is another example of the inability of a classical σ-donor ligand to stabilize a formally divalent osmium complex. We believe the difference in the case of hydrogen lies in the large polarizability of the metal hydrogen bond or—generally speaking—in its variability in bonding interactions that permits hydrogen to form complexes with metals having very different formal oxidation numbers. In contrast to the d^0 electron configuration in $[ReH_9]^{2-}$, a d^{10} configuration can be assumed in the $Mg_2Ni(O)H_4$, $Na_2Pd(O)H_2$, and $Li_2Pd(O)H_2$ hydrides (*11*, *12*). In between these extremes we have the still electron-rich d^8 $[PtH_4]^{2-}$ complex found in several hydrides by Prof. Brongers' group in Aachen; the corresponding $[PdH_4]^{2-}$ complex was also recently discovered in K_2PdH_4 (*13*, *14*). Octahedral d^6 complexes of the iron triad so far dominate the expanding number of these novel complex hydrides (*1–3*).

This work shows that metal hydride chemistry continues to be an interesting research field and that hydrogen is a very flexible ligand in transition metal chemistry, which is capable of stabilizing not only high formal oxidation states but also lower oxidation states, where we conventionally would expect to find ligands with good electron-accepting properties. In this aspect hydrogen is unique in homoleptic complexes, since no other ligand has been found that can stabilize such a large span of formal oxidation states.

Acknowledgments

This work has received support from the Swedish National Board for Technical Development. We are also indebted to Håkan Rundlöf for collecting the neutron diffraction pattern of Li_4OsD_6 at the R2 reactor in Studsvik.

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