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LETTERS TO THE EDITOR

Synthesis and Characterization of Ternary Alkaline-Earth Transition-Metal Hydrides Containing Octahedral $[Ru(II)H_6]^{4-}$ and $[Os(II)H_6]^{4-}$ Complexes

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Mg_2RuH_6, Ba_2RuH_6, Ca_2OsH_6, Sr_2OsH_6, and Ba_2OsH_6 with the K_2PtCl_6-type structure have been synthesized. Solid state IR spectroscopy applied to these and other, already known, ternary hydrides from the iron triad shows M–H stretching frequencies in the 1500–1850 cm^{-1} energy range, which are correlated with the size of the cube of counterions surrounding the complexes. Lower frequencies are found with larger counterions. The $\nu(M\text{–H})$ value increases on going from iron to osmium, indicating that H^- ions are well capable of stabilizing divalent osmium, which so far has been found exclusively with good electron-accepting ligands.

Introduction

In transition-metal hydride complexes, hydrogen is considered a pure σ-electron donor. The small size of hydrogen favors high coordination numbers and high formal oxidation states. Together with oxygen and fluorine, hydrogen is recognized for its ability to stabilize high oxidation states. When hydrogen has been found in connection with a low formal oxidation state, there has always been an ancillary ligand with good electron-accepting properties present (*1*). The increased interest in metal hydrides as hydrogen storage materials has, however, lead to the discovery of new ternary hydrides containing discrete anionic fragments of formally very low-valent homoleptic hydrogen complexes, counterbalanced by electropositive metal ions; examples are the formally zero-valent complexes $[NiH_4]^{4-}$ in Mg_2NiH_4 (*2*), and $[PdH_2]^{2-}$ in Li_2PdH_2 (*3*) and Na_2PdH_2 (*4*). These d^{10} complexes exist, although the usual stabilization mechanism for a low formal oxidation state, i.e., electron donation to suitable π^* or d orbitals on the ligand, is absent (*5*). Related to this also is the discovery of an octahedral $[Os(II)H_6]^{4-}$ complex in the ternary hydrides Mg_2OsH_6 (*6*) and Li_4OsH_6 (*7*). Formally divalent osmium complexes are known to exist only with ligands having good electron-accepting properties. The object of the present work has been to further investigate this transition metal to hydrogen bond in the iron triad, using IR spectros-

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copy. We chose to work on a series of ternary alkaline-earth transition-metal hydrides with the K_2PtCl_6 structure (*8, 9*). As a result we can also report on an addition to the number of known hydrides in this family by Mg_2RuH_6, Ba_2RuH_6, Ca_2OsH_6, Sr_2OsH_6, and Ba_2OsH_6. The corresponding ternary alkali hydrides (*7*) were unfortunately too reactive to allow us to bring them into suitable sample holders.

Raman spectroscopy would be another obvious method, but all our hydrides were quickly decomposed by the intense laser irradiation (Kr 15,453.7 cm^{-1} and Ar 19,436.4 cm^{-1}).

Synthesis and Structural Characterization

All hydrides were synthesized by the direct reaction of a powdered mixture of the alkaline-earth hydride and the transition metal in hydrogen at elevated temperatures and pressures, as has been described earlier for Mg_2OsH_6 and Li_4OsH_6 (*6, 7, 10*). The ternary calcium and strontium hydrides needed a higher reaction temperature of above 700°C, at 60 bar, to complete the reactions within a reasonable time, as compared with 480°C for Mg_2RuH_6 and Mg_2OsH_6. With barium hydride the reactions could be performed close to 600°C, and it is interesting to note how the reaction temperature reflects the thermal stability of the binary hydrides. It took 3–5 days to produce a reasonably single-phase sample of the ruthenium ternaries and about twice as long for the osmium analogues. The span in reaction time reflects an increasing inertness toward reaction with increasing size of the alkaline earth ion. The ternary hydrides, and especially the osmium-based ones, were oxygen- and moisture-sensitive, and the samples were handled in an argon atmosphere glove box. After synthesis, the reaction products were checked by Guinier–Hägg X-ray diffraction, and usually several syntheses had to be made to optimize the reaction yield, as indicated above. The X-ray films were evaluated according to Ref. (*7*).

The simplicity of the structure implies that no adjustable metal atom position parameters are necessary to describe the well-separated peak intensities in the X-ray patterns. So the structure of the novel hydrides could be confirmed by refining the fixed K_2PtCl_6 metal atom structure against the measured patterns, neglecting the weak X-ray scattering from the hydrogen atoms. The results are summarized in Table I. The structures were further checked by synthesizing the corresponding deuterides of the extremes of Table I, i.e., Mg_2RuD_6, Ba_2RuD_6, and Ba_2OsD_6, so that also the hydrogen positions could be verified with neutron diffraction. The results are given in Table II.

IR Spectroscopy

All spectra were recorded on a Polaris FT-IR spectrometer (Mattson Instrument Inc.) with a resolution of 2 cm^{-1}, typically in the 400–3200 cm^{-1} range. The hydrides were protected by outer layers of Spec-pure KBr (dried at 130°C in vacuum) in three-layer sample discs compacted in argon, with the inner layer being a mixture of sample and KBr.

The two bands allowed by octahedral symmetry dominated the IR spectra, a stretching mode with higher intensity in the 1500–1850 cm^{-1} energy range and a bending mode with lower intensity in the 700–900 cm^{-1} range, as can be seen in Fig. 1 for Mg_2OsH_6. If the stretching frequencies listed in Table III are plotted as a function of unit cell dimension, we can summarize the salient features of this work (cf. Fig. 2).

First, the vibrational frequency is strongly dependent on the unit cell dimension, i.e., the counterion radius. If we add the corresponding values from Eu_2RuH_6 and Yb_2RuH_6, taken from Ref. (*10*), they fall on the same curve, indicating that the electro-

TABLE I

OBSERVED d-VALUES, INTENSITIES, AND UNIT CELL DIMENSIONS FOR THE NEW TERNARY HYDRIDES, FROM GUINIER–HÄGG X-RAY DATA OBTAINED WITH Cu$K\alpha_1$ RADIATION (λ = 1.5405981 Å) AND WITH SILICON AS THE INTERNAL STANDARD AT 293 K

	Ca_2OsH_6		Sr_2OsH_6		Ba_2OsH_6		Mg_2RuH_6		Ba_2RuH_6	
hkl	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}
111	4.1905	1415	4.4057	4068	4.6544	391	3.8501	2782	4.6476	372
200	3.6264	130	—	—	—	—	3.3297	372	4.0204	352
220	2.5638	1598	2.6996	9059	2.8461	1276	2.3529	3015	2.8390	2314
311	2.1862	881	2.3015	2385	2.4283	212	2.0062	1493	2.4202	181
222	2.0934	49	—	—	—	—	—	—	2.3173	152
400	1.8129	284	1.9084	1255	2.0125	210	1.6636	482	2.0062	367
331	1.6638	396	1.7515	910	1.8470	66	1.5268	695	1.8422	65
420	1.6215	108	—	—	—	—	1.4883	210	1.7947	176
422	1.4806	680	1.5578	3950	1.6427	443	—	—	—	—
511,333	1.3960	345	1.4689	704	1.5475	51	1.2810	655	1.5447	88
440	1.2823	231	1.3489	926	1.4222	175	1.1767	532	1.4195	277
531	1.2260	466	1.2898	977	—	—	1.1251	1058	—	—
600	—	—	—	—	—	—	—	—	1.3382	113
620	1.1468	482	—	—	1.2722	199	—	—	1.2698	533
533	—	—	1.1639	122	—	—	—	—	—	—
622	—	—	—	—	—	—	—	—	1.2107	62
444	—	—	—	—	—	—	—	—	1.1587	49
551,771	—	—	—	—	—	—	—	—	1.1239	92
640	—	—	—	—	—	—	—	—	1.1132	42
	a = 7.2530(2) Å M_{13} = 114 R_F = 4.83%		a = 7.6319(9) Å M_{10} = 68 R_F = 8.30%		a = 8.0460(10) Å M_9 = 31 R_F = 3.71%		a = 6.6561(3) Å M_{10} = 96 R_F = 8.60%		a = 8.0283(5) Å M_{16} = 36 R_F = 6.52%	

Note. The R_F values obtained are based on a refinement of the antifluorite metal atom structure in the K_2PtCl_6-type framework, by using the SHELX program (*13*).

positivity of the counterion is of secondary importance. We further remeasured the IR spectrum of Mg_2FeH_6. The stretching frequency of 1750 cm^{-1} was in good agreement with Ref. (*11*). Adding this value to Fig. 2, we get the same trend for our metal–hydrogen bond as for the metal–carbon bond in the hexacyano complex in $K_4M(CN)_6$ (M = Fe, Ru, Os); i.e., the increase in metal–carbon bond strength from iron to osmium can be correlated with a decrease in the carbon–nitrogen bond strength as electrons are donated into its π^* orbitals on the ligand (*12*). Even without this stabilizing mechanism, the same behavior can be observed for the homoleptic hydrogen complexes in the iron triad. This fact, and also the existence of the formally zero-valent homoleptic hydrogen complexes mentioned above, is evidence for hydrogen having certain electron-accepting properties.

We attribute this to the large polarizability of the metal–hydrogen bond which permits hydrogen to distribute electron density away from the proximity of the central atom by means of its potential to adopt a large radius. This effect has not been fully appreciated, due much to the limitations of the conventional models for describing the oxidation state by formally counting the

TABLE II

POSITIONAL PARAMETERS AND ISOTROPIC TEMPERATURE FACTORS FOR Mg_2RuD_6, Ba_2RuD_6, AND Ba_2OsD_6 IN SPACE GROUP $Fm\bar{3}m$ (225), $Z = 4$

Atom	Site	Position		
		x	y	z
Ru, Os	4*a*	0	0	0
Mg, Ba	8*e*	1/4	1/4	1/4
D	24*e*	x_D	0	0

Mg_2RuD_6	Ba_2RuD_6	Ba_2OsD_6
$a^a = 6.6409(9)$ Å	$a = 8.0166(7)$ Å	$a = 8.0357(4)$ Å
$x_D = 0.251(2)$	$x_D = 0.215(2)$	$x_D = 0.221(3)$
Ru-D = 1.67(1) Å	Ru-D = 1.73(1) Å	Os-D = 1.77(2) Å
$B_{Ru} = 1.5(2)$ Å^2	$B_{Ru} = 1.5(4)$ Å^2	$B_{Os} = 0.9(3)$ Å^2
$B_{Mg} = 2.9(3)$ Å^2	$B_{Ba} = 1.9(5)$ Å^2	$B_{Ba} = 1.5(4)$ Å^2
$B_D = 0.8(2)$ Å^2	$B_D = 2.6(3)$ Å^2	$B_D = 2.8(3)$ Å^2

hkl	I_{calc}	I_{obs}	I_{calc}	I_{obs}	I_{calc}	I_{obs}
111	495	363	2182	2217	3933	3964
002	670	527	677	689	1242	1292
022	—	—	245	243	964	872
113	—	—	227	264	900	959
222	4742	4737	—	—	—	—
400	4572	4829	—	—	—	—
331	264	151	35	92	27	169
420	670	835	219	157	414	526
422	1	15	88	119	—	—
511	104	53	1473	1403	2325	2422
333	65	33	96	92	23	23
440	4332	4209	—	—	—	—
531	—	—	911	1021	—	—
600	—	—	170	127	—	—
442	—	—	49	37	—	—
620	—	—	555	703	1438	1761
622	—	—	—	—	1125	1117
444	—	—	675	643	1646	1813
711	—	—	—	—	157	138
551	—	—	—	—	1749	1544
640	—	—	—	—	206	499
642	—	—	660	639	—	—

Mg_2RuD_6	Ba_2RuD_6	Ba_2OsD_6
Bragg $R = 6.66$	Bragg $R = 7.37$	Bragg $R = 7.80$
$R_F = 5.18$	$R_F = 6.65$	$R_F = 8.29$
$R_{WP} = 8.91$	$R_{WP} = 9.71$	$R_{WP} = 12.12$

Note. The calculated and observed intensities are based on neutron diffraction data recorded at the R2 reactor in Studsvik, with a neutron wavelength of 1.470 Å at 293 K. The Rietveld refinement program DBW3.2S (*14*) was used in the evaluation. The temperature parameters are given as $B_{iso} = 8\pi^2\langle u^2\rangle$, where $\langle u^2\rangle$ is the mean-square amplitude of vibration. A few reflections had to be excluded as they were overlapped by the Bragg peaks from the aluminium sample holder (ϕ = 5 mm). The Ba_2OsD_6 solution was further hampered by the difficulty of getting a fully reacted sample.

[a] The unit cell dimensions were determined with X-ray diffraction similarly to Table I.

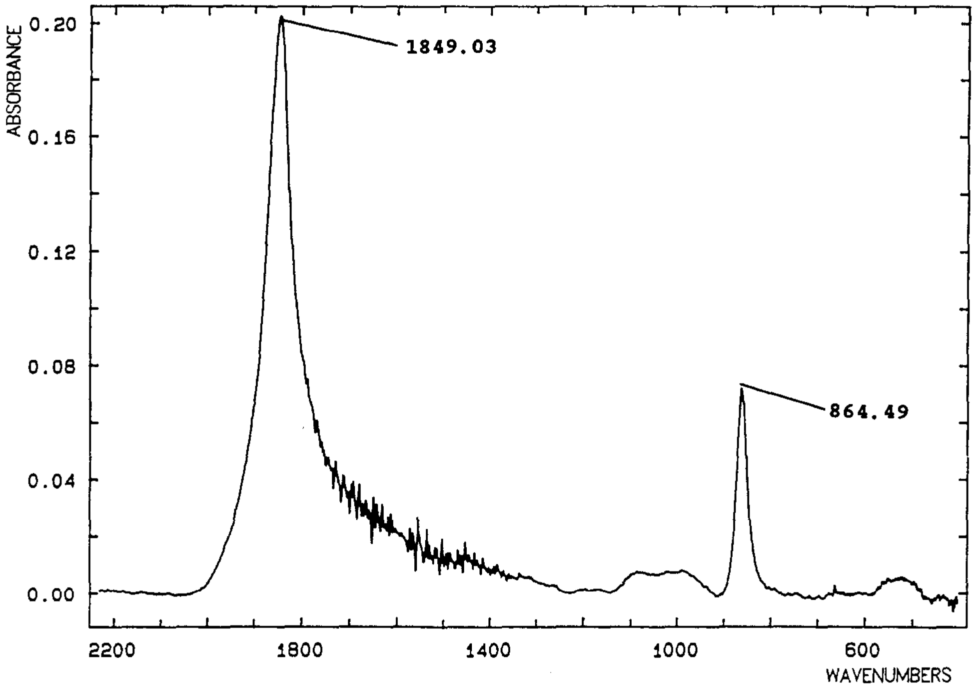

FIG. 1. Infrared spectrum of Mg_2OsH_6.

electrons, neglecting the fact that the real electron population in the valence shell of a transition metal is very like that of its atomic state. But it is likely that this small electron-accepting capacity (in absolute terms) is enough to stabilize the central atom in what conventionally would correspond to a low formal oxidation state. The large H^- ion

TABLE III

CUBIC UNIT CELL LENGTHS, a, AND THE IR STRETCHING FREQUENCIES, ν(M–H) AND ν(M–D), FOR THE TWO HYDROGEN ISOTOPES IN THE OCTAHEDRAL COMPLEXES

Hydride	a(Å)	$\nu(M\text{-H})$ (cm^{-1})	$\nu(M\text{-D})$	$\frac{\nu_H}{\nu_D}$
Mg_2RuH_6	6.6561(3)[a]	1783	1279	1.394
Ca_2RuH_6	7.2269(3)[a]	1559		
Sr_2RuH_6	7.6088(3)	1482		
Ba_2RuH_6	8.0283(5)	1438	1023	1.406
Yb_2RuH_6	7.248	1550 (9)		
Eu_2RuH_6	7.566	1480		
Mg_2OsH_6	6.6828(6) (6)	1849	1325	1.395
Ca_2OsH_6	7.2530(2)	1637		
Sr_2OsH_6	7.6319(4)	1575		
Ba_2OsH_6	8.0460(10)	1505	1078	1.396

Note. The ratio ν_H/ν_D is the shift in stretching frequency upon isotopic substitution.

[a] Redetermined in this work.

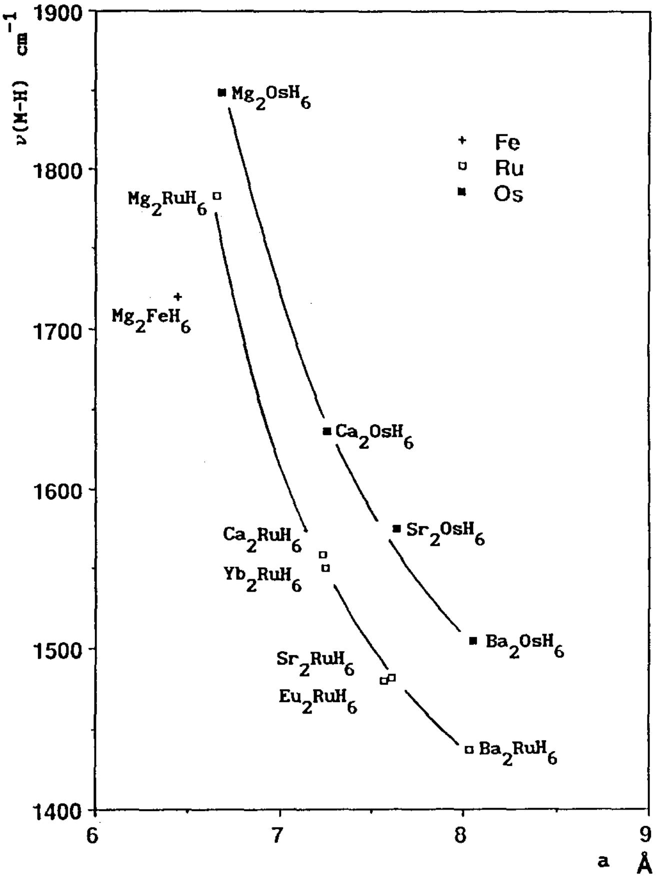

FIG. 2. Infrared stretching frequency, $\nu(M\text{-H})$, as a function of cubic unit cell length, a. The lines are only a guide for the eye.

would also be very sensitive to the spatial correlation of any charged counterion in the vicinity of the complex, as can indeed be observed in Fig. 2.

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