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Ternary Hydrides of Calcium and Strontium with Iridium, Rhodium and Ruthenium

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The ternary hydrides, Ca_2IrH_5, Sr_2IrH_5, Ca_2RhH_5, Sr_2RhH_5, Ca_2RuH_6, and Sr_2RuH_6 have been prepared. In each case the alkaline earth hydride was reacted with a Group VIII metal at high temperatures under a hydrogen atmosphere. X-Ray powder data showed that the two metal atoms are arranged in the fluorite structure. Powder neutron diffraction showed that the hydrogens octahedrally coordinate the Group VIII metal atom. Random vacancies of hydrogen sites were indicated for the iridium compound. The elemental analyses and magnetic susceptibility data support the structural assignments.

Introduction

The class of ternary hydrides or complex hydrides consisting of two metals and hydrogen is a small but growing family. The best known is $LiAlH_4$. Lithium forms ternary hydrides with a number of other metal atoms. Farr (*1*) and Lundberg et al. (*2*) reported on Li_4RhH_4 and Li_4RhH_5. Graefe and Robenson (*3*) reported reactions between lithium hydride and rhodium, iridium, palladium, and platinum. Chang (*4*) in his doctoral dissertation did a preliminary survey on the feasibility of a large number of ternary systems containing lithium. Liu and Magee (*5*) recently made a preliminary report on the Li–Pd–H system. The best known of the potassium ternary hydrides is K_2ReH_9 (*6*). Ashby et al. (*7*) synthesized $KMgH_3$. Reilly and Wiswall (*8*) found that magnesium and nickel form Mg_2NiH_4. Nickel also reacts with zirconium (*9, 10*) to form $ZrNiH_3$. Messer et al. (*11, 12*) reported the identification of $SrLiH_3$, $BaLiH_3$, and $EuLiH_3$. These were reported to have the perovskite structure. In part, it has been the curiosity about the hydride–oxide analogy and the hydride–fluoride analogy (*13*) that led to the investigation of alkaline earth, platinum group metal hydrides. A preliminary report on our results with strontium iridium hydride has already been published (*14*). We now wish to report the results of an extension of that study which includes the synthesis and characterization of ternary hydrides of calcium and strontium with ruthenium, iridium and rhodium.

Experimental

Calcium and strontium were purified by distillation under vacuum in a steel apparatus. Calcium was distilled at 800° and strontium at 925°. Hydrogen was Matheson extra dry or prepurified grade further purified by passing through a palladium tube in a Bishop hydrogen diffusion cell Model No. A-1-D. Calcium hydride and strontium hydride were synthesized by direct combination of the elements at 500°. The X-ray powder diffraction data for both calcium and strontium hydrides agreed with that reported by earlier workers (*15*). The hydrides were analyzed further for hydridic hydrogen by hydrolysis. A typical analysis for percent hydrogen for calcium hydride was determined to be 4.69%,

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calculated 4.79%; determined for strontium hydride 2.21%, calculated 2.25%.

The ternary hydrides were prepared by (a) combining the alkaline earth hydride and platinum metal powders in a 2:1 molar ratio, (b) tumble mixing the powders in a 1-dram polyethylene vial by manual rotation in all directions, (c) compressing the mixture into a cylindrical pellet 0.25 inch in diameter and 0.125–0.25 inch in length with a standard metallurgical pellet press at 5000 psi, (d) placing the pellet into a copper or molybdenum boat, (e) attaching the reaction tube containing the loaded boat to the vacuum line, (f) evacuating the system to 1×10^{-5} mm of pressure, (g) introducing the oxygen-free hydrogen through a palladium tube filter to a pressure of 631–658 mm, and (h) heating to 800° for 12 hr. All samples were handled in glove bags under a protective atmosphere of nitrogen.

No method could be found for purifying the ternary hydrides. No unreactive solvent could be found for recrystallizations. Fractional sublimation or selective decompositions of impurities was tried and found to be unsuccessful. In all cases, the decomposition point or sublimation temperature of possible impurities were too close to the decomposition temperature of the ternary hydrides.

An unsuccessful attempt was made to synthesize a single crystal for X-ray studies. Because these ternary hydrides decompose without melting, a sample of strontium iridium hydride was tamped into a gold thimble which was approximately $\frac{1}{8}$ inch in diameter and $\frac{1}{2}$ inch long. The thimble was then crimped and heated to 800° at about 65 kbar of pressure. The thimble on opening yielded a light-grey powder instead of the dark-colored starting material and furthermore showed very little hydridic hydrogen by hydrolysis.

The X-ray diffraction data were obtained by Debye–Scherrer techniques using glass capillaries sealed under nitrogen as well as with a General Electric XRD-5 diffractometer using vaseline-coated powder on a standard microscope slide. The agreement of the two methods indicated that the vaseline protects the powder from hydrolysis for the time it takes to complete a diffractometer run. The intensities of the diffractometer reflections were determined by cutting the tracing above the background and weighing the paper on an analytical balance.

The neutron diffraction intensities were measured on a two-axis neutron spectrometer using a wavelength of 1.06_4 Å. The samples were sealed into a $\frac{3}{8}$-inch i.d. cylindrical quartz tube. A quartz pattern was subtracted from the diffraction pattern. The data from the iridium compound were corrected for absorption.

Densities were calculated by the liquid buoyancy method using reagent grade carbon tetrachloride previously dried over calcium hydride. For these determinations, the powder was compressed at 5000 psi into a cylindrical shaped pellet, submerged in the carbon tetrachloride, deaerated with partial vacuum, and the weight determined. The standard deviation based on five samples was 0.1 g/ml.

Routine elemental analyses were carried out for the alkaline earth and Group VIII metals. Strontium was analyzed as the insoluble sulfate and calcium was analyzed as the insoluble oxalate (*16*, *17*). The Group VIII metals were determined gravimetrically as the metals after complete hydrolysis. The X-ray powder pattern confirmed these residues after hydrolysis to be the metal powder. An additional check was made by titrating the base resulting from the hydrolysis of the hydride with standard 0.1 N HCl to a phenolphthalein end point.

The hydrogen analyses were the most difficult of all. In the earlier work, complete reliance was placed on the hydrolytic determination for hydridic hydrogens. When pyrolytic decomposition showed a discrepency with the early hydrolytic determinations, the results for pyrolytic decompositions always being higher than the hydrolytic determinations, both methods were refined. Hydridic hydrogen was determined hydrolytically by weighing out 0.07–0.15 moles of the ternary hydride into a reaction tube. This tube was then evacuated and water distilled under vacuum. On removing the liquid nitrogen trap, the ice melted and reacted with the ternary hydride generating hydrogen. The hydrogen was transferred with a Toepler pump into a calibrated volume. The purity was checked each time by mass spectrometry. Pyrolytic decompositions were carried out by placing 0.07–0.15 mmoles of the ternary hydride in a 3.5-cm molybdenum sleeve inside a quartz sleeve which in turn was placed in a horizontal quartz tube attached to a standard vacuum system. The sample was then heated to 890° until no more gas was evolved, which was generally within 1 hr. The gas was transferred as it was evolved to a calibrated volume using a Toepler pump. The possibility of an air leak was monitored by checking the collected sample for purity by mass spectrometry. Several samples analyzed by hydrolytic and pyrolytic methods were submitted for hydrogen analysis by classical combustion methods to Baron Consulting Co., Orange, Conn.

Magnetic susceptibilities were measured by the Guoy method using a magnet with pole faces 5 cm in diameter and 4 cm apart. The instrument was powered with a Sorensen Norbatron Model DCR 80-10 Power Supply. The measurements were made over a temperature range of −196° to room temperature.

Differential thermal analyses were performed on a DuPont 1200 high temperature apparatus, modified to allow either vacuum operation or a 225 ml/min flow rate of hydrogen gas at 1 atm. pressure. Scans were carried out at either a 10°/min or more generally 20°/min heating rate over a temperature range of room temperature to 900°. Platinum cup sample holders were used with alumina as the reference standard.

The electrical resistivity of the ternary hydrides was crudely determined. A sample of powder was compressed at 5000 psi into a pellet about ¼ inch in diameter. The two probes were placed on opposite faces of the pellet and the electrical resistance was measured with a Triplett voltmeter Model No. 369.

Results

The ternary hydrides are crystalline nonvolatile solids reactive to water and acids and insoluble in common organic solvents. The ternary hydrides of iridium and rhodium are black and those of ruthenium are light green.

The 2:1 molar ratio for the alkaline earth and platinum group metal was originally determined for the strontium iridium hydride by varying the ratio of the strontium hydride and iridium reactants. At ratios of strontium hydride to iridium greater than 3:1, excess strontium hydride could be detected in the powder pattern. At strontium hydride to iridium ratios of 5:3 and less, excess iridium could be detected in the powder pattern. Since the analysis for strontium and iridium showed that the amount used for the reaction was still present in the product, the interpretation of the powder pattern was used to confirm our prejudice for the 2:1 molar ratio. The isomorphous structure for strontium ruthenium, strontium rhodium, calcium iridium, calcium ruthenium and calcium rhodium hydrides as indicated by the powder patterns was used to assign the same stoichiometry for these compounds.

The determination for the amount of hydrogen present in the final product was more troublesome. At first, hydrogen uptake during reaction was used as

TABLE I

HYDROGEN ANALYSES

M–*M'*–H[a]	H basis[b]	Hydrolysis trials (mmoles H/mmoles sample)			Pyrolysis trials (mmoles H/mmoles sample)			H used in reaction	Av. hydrolysis/ av. pyrolysis	Av. pyrolysis/ H used	Combustion analyses
		1	2	3	1	2	3				
Sr–Ir–H	5	4.61	4.57		5.15	5.10		$Sr_2IrH_{4.89}$	0.90	1.04	$Sr_2IrH_{5.11\pm.3}$
	6	4.99	4.95		5.16	5.11			0.97	1.05	
Sr–Rh–H	5	4.43	4.16	4.09	4.50	4.56	4.53	$Sr_2RhH_{4.70}$	0.93	0.96	
	6	4.45	4.17	4.10	4.52	4.58	4.55		0.93	0.97	
Sr–Ru–H	5	5.30	5.30		6.00	5.95		$Sr_2RuH_{5.80}$	0.89	1.03	$Sr_2RuH_{5.75\pm.3}$
	6	5.75	5.75		6.02	5.98			0.96	1.03	
Ca–Ir–H	5	4.02	3.70	3.80	4.46	4.62	4.60	$Ca_2IrH_{4.81}$	0.83	0.96	$Ca_2IrH_{4.38\pm.3}$
	6	4.03	3.72	3.82	4.48	4.63	4.62		0.83	0.96	
Ca–Rh–H	5	4.14	4.12	4.03	4.89	4.89	4.97	$Ca_2RhH_{5.30}$	0.83	0.93	
	6	4.17	4.14	4.05	4.91	4.91	4.99		0.83	0.93	
Ca–Ru–H	5	4.19	4.13		5.25	5.63	5.86	$Ca_2RuH_{6.07}$	0.75	0.92	
	6	4.21	4.16		5.28	5.66	5.89		0.75	0.92	
Ca–Ru–H	5	4.20	4.43		5.99	5.77	5.96	$Ca_2RuH_{6.28}$	0.73	0.94	
	6	4.18	4.45		6.03	5.80	5.99		0.73	0.95	
Ca–Ir–H	5	3.79	3.70	3.77	4.98	5.13			0.74		
	6	3.81	3.71	3.79	5.00	5.14			0.74		

[a] In general, each compound listed indicates a separate preparation.

[b] mmoles of sample is calculated on the basis of five or six hydrogens.

a criterion. However, a scattering of values was traced to hydrogen leaking from the apparatus. The main trouble seemed to be the greased joint attaching the quartz reaction tube to the vacuum system. This problem was eventually solved by using a water-cooled joint. The uptake values then became more consistent and were consonant with the other hydrogen determinations. As shown in Table I, the hydrolysis results are generally lower than either the pyrolysis or uptake values. Because strontium hydride as well as the other common binary hydrides can be analyzed by the same technique, it was postulated that some of the hydrogen might be trapped in the Group VIII metal. Two experiments were carried out to show that this was not the case. Pyrolysis following hydrolysis showed no additional hydrogen. Hydrolysis of a mixture of a Group VIII metal and the binary alkaline earth hydride yielded the same results as those obtained for the hydrolysis of the binary hydride alone. Calculations for the hydrolytic determination assume that each molecule of hydrogen is formed from a negative hydrogen from the hydride and a positive hydrogen from water. If an appreciable decomposition of the hydride occurs during hydrolysis so that there is a "pyrolysis" reaction competing with the hydrolysis reaction, the values determined would be low. In order to test this, the ternary deuteride was prepared and hydrolyzed with ordinary water. The collected gas, analyzed by mass spectrometry, showed 50% deuterium. At the present time, the reason for the low hydrolytic results have remained unexplained.

The analyses for the calcium and Group VIII metal was straightforward. The representative results are shown in Table II.

TABLE II

METALLIC ELEMENTAL ANALYSIS

Compound	Element	Calculated %	Found %
Ca_2IrH_x	Ca	28.9	27.2
	Ir	69.7	70.4
Sr_2IrH_x	Sr	47.2	45.6
	Ir	51.8	52.7
Ca_2RhH_x	Ca	43.0	41.5
	Rh	55.0	57.3
Sr_2RhH_x	Sr	62.0	60.4
	Rh	36.7	37.4
Ca_2RuH_x	Ca	43.0	40.7
	Ru	55.0	56.2
Sr_2RuH_x	Sr	62.0	60.5
	Ru	36.7	37.3

The X-ray powder patterns of the ternary hydride systems being described were indexed on the basis of a face-centered cubic cell. A structure factor analysis of the ternary hydrides was found to be consistent with the space group *Fm*3*m*. A computer program prepared by Busing–Levy adapted for the IBM 360 computer was used to calculate the F^2 values (*18*). The atoms with exception of hydrogen were assigned to the fluorite structure, i.e., the alkaline earth atoms were placed in the fourfold positions and the Group VIII metal in the eightfold positions. Table III shows the results of this analysis. In the case of calcium rhodium hydride and strontium ruthenium hydride, the temperature factors were not included in calculating the intensity values. Also submitted are the reliability factors calculated as follows:

$$(R) = \frac{\Sigma|I_0 - kI_c|}{\Sigma I_0}.$$

The density measurements were consistent with four molecules per unit cell. Experimental and calculated values are reported in Table IV.

Neutron diffraction patterns were determined for strontium iridium deuteride and strontium ruthenium deuteride. Although the analyses for deuterium were carried out before the refinement of the analytical procedures for hydrogen, it is felt that the stoichiometry determined would be found to be of the order of that determined for the ^1H isotope as shown in Table I. The neutron diffraction pattern for both ternaries showed that the face-centered translations and cubic symmetry arguments derived from the X-ray data were not violated by the deuterium atoms. The very strong 400 reflection for Sr_2IrD_x indicated that an X coordinate for deuterium was not too far from $\frac{1}{4}$ or $\frac{1}{2}$, i.e., it had to have a large positive contribution. The assignment of the deuterium to $(\frac{1}{4}, \frac{1}{4}, 0)$ was tried as was $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(X, 0, 0)$ where X was approximately 0.25. The third possibility gave the most satisfactory data fits. The deuterium atoms in the ruthenium compound were found to occupy the same octahedral $(0, X, 0)$ sites about the ruthenium atom as was found for the iridium compound. The results of the final refinement, together with all pertinent crystal data, are given in Table V.

Calculated and observed sums of F^2 for each measurement from a least-squares refinement on single intensities are given in Table VI together with the standard deviation of each measurement, the scale is arbitrary. In each case $R = \Sigma|jF_0^2 - jF_c^2|/\Sigma jF_0^2 = 0.09$, where j is the multiplicity of the diffraction peak. If σ (jF^2) is substituted for the numerator, an R (expected) $= 0.08$ is obtained.

Standard deviations of the metal-deuterium bonds

TABLE III

Observed and Calculated X-Ray Intensities

	Ca_2IrH_5		Sr_2IrH_5		Ca_2RhH_5		Sr_2RhH_5		Ca_2RuH_6		Sr_2RuH_6	
hkl	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd[a]	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd[a]
111	100	100	59.7	63.4	35.5	73.8	31.5	33.3	67.7	76.0	27.6	33.1
200	11.2	15.6	0	0	5.7	13.8	5.6	8.1			8.0	8.9
220	85.5	80.4	100	100	100	100	100	100	100	100	100	100
311	46.1	45.0	35.3	33.3	22.6	38.4	16.4	16.3	36.9	36.5	26.3	17.7
222	1.3	4.0	0	0			3.6	2.1			4.5	2.4
400	9.8	11.8	17.8	17.0	17.3	17.1	16.4	15.8	16.3	15.5	20.0	17.7
331	14.9	16.1	12.8	13.9	8.3	16.3	6.3	6.6	15.8	14.0	10.0	7.3
420	3.0	4.8			1.6	8.3	1.9	2.5			3.6	3.3
422	20.0	18.9	32.6	33.2	28.4	32.3	37.8	30.0	28.9	26.5	40.6	35.8
511, 333	9.2	9.3	9.9	10.0	6.5	12.1	4.4	4.6	10.7	9.3	5.5	5.3
440	5.0	4.6	10.9	9.7	8.3	9.5	11.9	8.6	6.6	7.1	12.2	10.9
531	8.4	8.2	8.7	9.3	5.1	11.9	5.3	4.2	9.7	5.4	5.3	5.2
620	3.6	6.0	11.7	13.0	11.3	13.6	12.4	11.3	9.2	9.2	16.5	15.2
533	1.7	2.6	2.1	3.3	1.6	3.2			1.7	2.0		
444	1.9	2.2	3.1	3.2	2.2	3.7	2.9	2.8	3.4	2.3	5.7	4.0
551, 711	4.0	3.7	4.4	5.1	3.6	7.7			5.1	4.6		
642	9.3	5.7	12.7	10.3	13.7	20.5	17.1	13.7	12.1	11.7	22.7	20.5
553, 731	8.0	4.4	4.1	6.5	4.6	11.1			7.0	5.9	4.6	4.0
660, 822	7.4	3.4	10.4	10.3	12.1	18.5	11.0	9.1	8.3	5.9	15.3	15.6
751, 555	1.2	2.9	4.4	5.0	3.4	11.3			6.1	5.1		
840			7.3	5.1	10.7	17.0	7.4	6.6	8.3	10.1		
911, 753			6.1	7.2								
	$R = 0.10$		$R = 0.06$		$R = 0.45$		$R = 0.09$		$R = 0.08$		$R = 0.11$	

[a] No temperature correction.

are about 0.02 Å for the iridium compound and 0.01 Å for the ruthenium. These are probably somewhat low. One may note in Table VI that excellent low angle agreement, especially for the ruthenium compound, between observed and calculated intensities becomes much poorer at high angles. This is obviously due to the weighting that took into account the higher accuracy of the low angle reflections. In fact, only the deviation of the observed from calculated 642 reflection for the ruthenium compound is outside 2σ. Reweighting to fit 642 exactly will push M towards the origin by $\simeq 0.04$ Å. Alternatively, refining the deuterium with anisotropic thermal parameters will give a better fit. Here, however, the rms amplitude component along the X axis went negative by one standard deviation. Since such a vibration is physically impossible, it was decided to accept the result weighted by counting statistics with isotropic thermal parameters as that derived from the most rigorous procedure and accept a maximum error of 0.04 Å in the M–D distance.

TABLE IV

Density Data

		Density (g/cc)	
System	Cell dimension[a]	Experimental	Calculated
Ca–Ir–H	7.29	4.80	4.85
Sr–Ir–H	7.62	5.46	5.56
Ca–Rh–H	7.24	3.40	3.31
Sr–Rh–H	7.60	4.20	4.24
Ca–Ru–H	7.24	3.32	3.31
Sr–Ru–H	7.60	4.25	4.24

[a] Cubic cell.

Magnetic susceptibility measurements showed that these ternary hydrides are either very weakly paramagnetic or diamagnetic. All gave evidence of

TABLE V

STRUCTURAL AND THERMAL PARAMETERS AND CRYSTALLOGRAPHIC DATA FOR Sr_2IrD_5 AND Sr_2RuD_6 (SPACE GROUP *Fm*3*m*)

Atom	Positions[a]	Multiplicity
Sr	$\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	8
Ir, Ru	(0,0,0)	4
D	$\pm(X,0,0)$ $\pm(0,X,0)$ $\pm(0,0,X)$	24

[a] Plus face centering, i.e., $(0,\frac{1}{2},\frac{1}{2})$ and permutations should be added to each atomic position:

		Sr_2IrD_5[b,c]	Sr_2RuD_6[b,c]
		$a = 7.62$ Å	7.60 (lattice parameter)
Sr		$b = 0.656 \times 10^{-12}$ cm	0.656×10^{-12} cm (scattering length)
		$B = 0.3\ (0.3)\ A^2$	0.0 (0.3) (Debye–Waller factor)
Ir, Ru		$b = 2.4\ (0.5)$	0.73
		$B = 1.8\ (0.3)$	1.0
D		$b = 0.603$	0.613
		$X = 0.233\ (0.002)$	0.223 (0.001)
		$B = 1.6\ (0.2)$	0.9 (0.2)

Atoms D/atom Ir = 5.0 (0.3)

[b] Standard deviations are in parentheses and refer to the least significant figures.

[c] Assumes 98% deuteration for the iridium compound and 99.5% deuteration for the ruthenium compound.

TABLE VI

OBSERVED AND CALCULATED AMPLITUDES

	Sr_2RuD_5			Sr_2IrD_6		
hkl	jF^2 obsd	jF^2 calcd	σ	jF^2 obsd	jF^2 calcd	σ
111	32	35	2	95	95	6
200	7	7	2	18	16	2
220	26	25	3	119	127	8
311	13	14	4	86	79	9
222	320	321	7	392	391	15
400	403	399	10	697	712	20
331	0	6	4	0	3	8
420	0	4	4	0	13	8
422	34	23	8	176	175	15
511 333	199	205	11	397	395	22
440	647	643	17	1091	1097	31
531 600 442	148	122	20	421	334	35
620	67	97	16	427	342	43
533 622	688	681	29	761	735	40
444	372	345	42	548	565	43
551 711 640	324	274	44	320	475	34
642	205	123	30	491	505	39
553 731	130	193	30	304	237	35
800	164	219	23	269	342	46

weak field dependence. A small field dependent magnetic susceptibility was observed for the strontium and calcium hydrides used as reactants. A possible source of ferromagnetic contamination is the steel distillation column used in the purification of strontium and calcium metals. In order to compensate for the ferromagnetic display, the magnetic susceptibility was measured at several field strengths. The extrapolation of the reciprocal of the field strength versus magnetic susceptibility to zero reciprocal field was such that it could not be definitely decided whether the ternary hydrides are diamagnetic or very weakly paramagnetic.

The magnetic behavior of each ternary was determined over a temperature range from −196° to room temperature. An essentially temperature-independent behavior was observed for the ternary systems of iridium and ruthenium. A small susceptibility decrease with increasing temperature was observed for the rhodium ternaries.

The electrical conductivity is reported in Table IX for each ternary hydride. A sharp departure in the electrical properties was noted for the rhodium ternary hydrides in comparison to those composed of iridium and ruthenium.

The results of the differential thermal analysis are shown in Tables X and XI. Table X indicates the behavior of the ternary hydride under conditions which might be used for syntheses. Table XI indicates the processes which take place when the ternary hydride is pyrolytically decomposed to analyze for hydrogen.

TABLE VII

BOND DISTANCES (IN Å) FOR THE Sr_2MD_x STRUCTURE

Bond	Iridium	Ruthenium
M–D	1.70	1.69
Sr–D	2.70	2.69
Sr–*M*	3.30	3.29

TABLE VIII

MAGNETIC SUSCEPTIBILITIES ($H^2 = 46.4 \times 10^6$ Oe^2)

Compound	Temp (°K)	Mag. Susc. ($\chi_m \times 10^6$)	Slope ($\chi_m \times 10^7$/°K)
Sr_2IrH_x[a]	269	15	−0.45
Ca_2IrH_x	300	20	−0.25
Sr_2RhH_x	296	38	−3.7
Ca_2RhH_x	297	31	−5.8
Sr_2RuH_x	296	−1.6	−0.7
Ca_2RuH_x	298	300	−1.8

[a] This sample measured at 33.4×10^6 Oe^2.

Discussion

The X-ray and neutron powder diffraction data indicate that the alkaline earth metal and the Group VIII metal are arranged in the fluorite structure with the alkaline earth metal tetrahedrally surrounded by the Group VIII metal. While the structure from the neutron diffraction work is not as precise as desired, there is no doubt about the general geometry. No other structure tested gave results that fit. Assuming the model structure to be correct, the overall data fit is very good; reflections calculated to be strong are strong and the weak ones are weak. In the model structure, the hydrogens are located two on each edge of the unit cell approximately $\frac{1}{4}$ in from the corners, four on each face of the unit cell approximately $\frac{1}{4}$ in from the middle of the edge and six in the octahedral cavity of the unit cell with the hydrogens octahedrally arranged and oriented symmetrically within the octahedral cavity. Each Group VIII metal is, therefore, surrounded by six hydrogens. Another way of describing the structure is to consider that it is composed of Sr^{2+} or Ca^{2+} ions and the octahedrally coordinated $(MH_6)^{4-}$ ions.

TABLE IX

ELECTRICAL CONDUCTIVITY

System	Specific conductivity (ohms^{-1} cm^{-1})
Ca–Ir–H	$<6.4 \times 10^{-8}$
Sr–Ir–H	$<2.6 \times 10^{-7}$
Ca–Rh–H	5.0×10^{-1}
Sr–Rh–H	2.6×10^{-1}
Ca–Ru–H	$<2.6 \times 10^{-7}$
Sr–Ru–H	$<6.4 \times 10^{-8}$

TABLE X

DIFFERENTIAL THERMAL ANALYSIS: HYDROGEN ATMOSPHERE

Sample M–M'–H	Endotherm temperatures (°C)	Exotherm temperatures (°C)
Ca–Ir–H		370 Broad 440–640 Rapid climb 710–860
Sr–Ir–H	Broad 305–365 Sharp 665 880	
Ca–Ru–H		605 700 775
Sr–Ru–H	Broad 410–495 Sharp decline Beginning 660	Short 105
Ca–Rh–H	360 390	Sharp 725
Sr–Rh–H	Broad 270–380 Sharp 815	Sharp 260

TABLE XI

DIFFERENTIAL THERMAL ANALYSIS: VACUUM

Sample M–M'–H	Endotherm temperature (°C)	Exotherm temperatures (°C)
Ca–Ir–H	Broad 310–360	190–310 550, 575, 620 655, 745
Sr–Ir–H	Large 300–360 Sharp 670 Broad 845–905 peaking at 880	180–210
Ca–Ru–H	Broad 95–260 Broad 640–765 Sharp 850	Broad 460–490 Sharp 840, 870
Sr–Ru–H	350 Rapid decline beginning 765	Broad 105–120 Sharp 285
Ca–Rh–H	Sharp 335 730	350, 370 Sharp 750
Sr–Rh–H	270 470	Broad 195–235 285, 310, 335, 360 Broad 685–805 peaking at 730

Refinement on deuterium occupancy led to the atomic ratio D/[Sr_2 and Ir] = 5.0 ± 0.3 with random vacancies.

The hydrogen analysis has been troublesome. Although several of the compounds analyze for six, or close to six, hydrogens per formula unit, some are distinctly lower. Two possibilities present themselves. Either this system is analogous to the lithium ternaries described by Farr and Magee (*1*, *2*), in that distinct phases similar to Li_4RhH_4 and Li_4RhH_5 are produced, or a defect structure is formed wherein there are random vacancies in the 24 hydrogen sites per unit cell. If there are two or more phases present, there should at least be a broadening of the X-ray lines at higher angles. Careful examination has not yielded an indication that this phenomena is occurring. We, therefore, favor the hypothesis that some of the sites are randomly vacant and a defect structure is being formed. This is in agreement with the neutron diffraction results on Sr_2IrD_5.

The magnetic susceptibility data would seem to argue against all of 24 hydrogen sites of the iridium and rhodium ternaries being occupied. For complete occupancy, the oxidation state of iridium and rhodium would have to be 2+ with electronic configurations of (Xe) $4f^{14}$ $5d^7$ and (Kr) $4d^7$, respectively. This would, of necessity, lead to paramagnetism. Since this type of behavior is not observed, it is proposed that the stoichiometry of the iridium and rhodium compounds be $M_2M'H_5$ and the ruthenium compound be $M_2M'H_6$. A 1+ oxidation state for iridium and rhodium leads to a contribution of eight electrons from the metal to the coordination sphere. One possible arrangement for these electrons is to pair them in the *d* orbitals leaving dsp^3 orbitals for the hydride ligands. This can be pictured as a square pyramid geometry randomly oriented in the crystal or, alternately, as an octahedral geometry with an electron pair occupying one of the octahedral sites. Either would satisfy the neutron diffraction data which indicates a defect structure in which the hydrogens are octahedrally arranged about the Group VIII metal with random absences. The 2+ oxidation state for ruthenium leads to a contribution of six electrons from the metal to the coordination sphere. This makes possible the placing of hydride ligands in d^2sp^3 orbitals. The ligand field picture for second- and third-row transition elements in the solid state is tenuous at best. The important argument is that the oxidation states proposed can account for diamagnetism. The hydrogen analyses support this proposition. Although the precision within a method is good, the agreement between methods is not as good. The difficulties of hydrogen analyses have been encountered by others (*6*) as well as ourselves. It now appears that the stoichiometry Sr_2IrH_4 which we reported in a note (*14*) is quite certainly low in hydrogen. The large numbers of analyses done since that date, however, satisfy us that our current postulates for the five and six hydrogens are essentially correct. This is further substantiated by the neutron diffraction work. Based on our model and the size of the unit cell, it is doubtful that there would be any metal–metal interactions in the ternary hydride which could be detected by magnetic susceptibility data.

Only some broad generalizations can be made from the DTA data. The results under vacuum indicate that the hydrogen comes off in stages. This was noted qualitatively in terms of the amount of hydrogen generated per time and temperature during pyrolytic analyses for the hydridic hydrogens. The DTA results in a hydrogen atmosphere show that at least one of the properties of the ternary hydrides is a function of the alkaline earth used. The fact that Ca–Ir–H and Ca–Ru–H show exotherms whereas Sr–Ir–H and Sr–Ru–H show endotherms indicates that if these are phase transitions of the ternary system, the calcium or strontium seem to affect the system quite differently.

A consideration of periodic properties immediately poses two questions. Does barium react similarly to calcium and strontium? Does osmium form ternary hydrides with calcium and strontium?

Barium hydride was reacted with ruthenium, rhodium and iridium. Barium hydride and iridium formed a light-brown solid, barium hydride and rhodium formed a black compound and barium hydride and ruthenium formed a bright green compound. The X-ray powder diffraction lines characteristic of the starting materials disappeared for the iridium and rhodium reactions. Weak lines were still visible in the ruthenium reaction. Hydridic hydrogen determinations indicated similar amounts of hydrogen as the calcium and strontium analogs. The X-ray powder diffraction lines for the new phase were so diffuse and weak that structural studies could not be carried out using the powder method.

Strontium hydride and osmium were reacted in a 2:1 molar ratio at 800° for 12 hr. New lines were observed indicative of a new phase, but unreacted starting materials were also observed. Increasing the temperature did not increase the yield of the new phase. Decreasing the reaction temperature and increasing the reaction time did seem to lower the amount of unreacted material. The synthesis of the osmium compound seems to be caught in the thermodynamics-kinetics bind. Work is being planned to try to find conditions for driving this reaction to completion.

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References

1. J. D. Farr, *J. Inorg. Nucl. Chem.* **14**, 202 (1960).
2. L. B. Lundberg, D. T. Cromer, and C. B. Magee, Abstracts, 155th. National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p. 147 M.
3. A. F. Graefe and R. K. Robenson, *J. Inorg. Nucl. Chem.* **29**, 2917 (1967).
4. F. C. Chang, Doctoral Dissertation, Univ. of Denver, 1968; "Ternary Hydride Phases Formed by Reaction of Lithium Hydride and Selected Metals", *Dissertation Abstracts B* **29**, 2459 (1969).
5. J. Liu and C. B. Magee, Abstracts, 160th. National Meeting of the American Chemical Society, Chicago, Ill., September 1970, Inor #25.
6. S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.* **3**, 558 (1964).
7. E. C. Ashby, R. Kovar, R. Arnott, *J. Amer. Chem. Soc.* **92**, 2182 (1970).
8. J. J. Reilly and R. H. Wiswall, Jr., *Inorg. Chem.* **7**, 2254 (1968).
9. G. G. Libowitz, H. F. Hayes, and T. R. P. Gibb, *J. Phys. Chem.* **62**, 76 (1958).
10. I. R. Tannenbaum, W. L. Korst, J. S. Mohl, and G. G. Libowitz, A. E. C. Report No. NAA-SR-7132, 1963.
11. C. E. Messer, J. C. Eastman, R. G. Mers, and A. J. Maeland, *Inorg. Chem.* **3**, 776 (1964).
12. C. E. Messer and K. Hardcastle, *Inorg. Chem.* **3**, 1327 (1964).
13. C. E. Messer, *J. Solid State Chem.* **2**, 144 (1970).
14. R. O. Moyer, R. Ward, L. Katz, and J. Tanaka, *Inorg. Chem.* **8**, 1010 (1969).
15. C. Zintl and A. Harder, *Z. Electrochemie* **41**, 41 (1935).
16. L. Erdey, "Gravimetric Analysis," Part II, p. 659, Pergamon Press, New York, 1965.
17. Ibid., p. 628.
18. W. R. Busing, K. O. Martin, and A. A. Levy, "A Fortran Crystallographic Least-Squares Program," Oak Ridge National Laboratory Union Carbide Corporation, United States Atomic Energy Commission, ORNL-TM-305, 1962.