$Ca_4Mg_4Co_3H_{19}$ and $Yb_4Mg_4Co_3H_{19}$, containing orientationally disordered square-pyramidal $[CoH_5]^{4-}$ anions

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Abstract

The title hydrides and their deuterides were synthesized by a solid state reaction at 790–800 K and 120–155 bar hydrogen (deuterium) pressure, and characterized by X-ray single-crystal (Ca compound) and neutron powder diffraction (Ca and Yb compounds). They crystallize with cubic symmetry, space group $P\bar{4}3m$, $Ca_4Mg_4Co_3H_{19}$: $a = 6.6953(2)$ Å, deuteride: 6.6809(2) Å; $Yb_4Mg_4Co_3H_{19}$: $a = 6.6727(2)$ Å, deuteride: 6.6591(1) Å ($T = 295$ K). The structures contain tetrahedrally coordinated D⁻ anions with bond distances [D3–Mg] = 1.912(5) Å (Ca) and 1.902(7) Å (Yb), [D3–3Ca)] = 2.355(6) Å and [D3–3Yb] = 2.354(5) Å, and square-pyramidal $[CoD_5]^{4-}$ complex anions in which the equatorial ligands are ordered with bond distances [Co–4D1] = 1.546(3) (Ca), 1.535(5) Å (Yb) and the apical ligands are disordered with bond distances [Co–D2] = 1.586(9) (Ca), 1.60(1) Å (Yb).

1. Introduction

Recently, we have reported iron-based quaternary metal hydrides of composition $M_4Mg_4Fe_3H_{22}$ (M = Ca, Yb) which contain octahedral $[FeH_6]^{4-}$ complexes and hydride anions H⁻ not bonded to the transition element [1,2]. Here we report on their cobalt-based analogues of composition $M_4Mg_4Co_3H_{19}$ (M = Ca, Yb) which contain square-pyramidal $[CoH_5]^{4-}$ complexes and H⁻ anions.

2. Experimental details

2.1. Synthesis

Binary alloys of nominal compositions MMg (M = Ca, Yb) were prepared from the elements (Ca: CERAC Inc., Milwaukee, WI, −4 mesh, 99.5%; Mg: CERAC, 1/8″ pieces, 99.99%; Yb: Alfa products, rod, 99.9%) by arc-melting, and powdered under protective argon atmosphere. Cobalt rods (Goodfellow, England, ϕ 5 mm, specpure) were placed in powder mixtures of

MMg and LiH (LiD) (Alfa products, 98%) which was added as a flux at a ratio of MMg:LiH = 4:1. The samples were wrapped into molybdenum foil and placed in a high-temperature high-pressure autoclave. After evacuating to about 10^{-5} bar and flushing with argon it was charged with hydrogen (deuterium) gas (H₂: Polygaz, Genève, Switzerland; 6N; D₂: AGA, 2N8) to an initial pressure of about 75 bar at room temperature. The temperature was increased to 790–800 K, yielding a hydrogen (deuterium) pressure of 155 bar, held at that temperature for 3–6 weeks (final pressure 120 bar), and then cooled to room temperature. After releasing the hydrogen (deuterium) pressure the autoclave was opened and the samples transferred to an argon-filled glove-box. The unreacted parts of cobalt and some small quantities of $M_4Mg_3H(D)_{14}$ [3,4] impurity phase were mechanically removed. The remaining products were black and stable in air.

Single crystals of $Ca_4Mg_4Co_3H_{19}$ were obtained from similar reaction conditions by increasing the LiH flux concentration to CaMg:LiH = 2:1. The crystals had a dark brownish colour and were translucent.

2.2. X-ray and neutron diffraction

The samples were characterized by X-ray powder diffraction at room temperature (Guinier camera, Co Kα radiation for Ca compound and Cu Kα_1 radiation for Yb compound, internal standard: silicon powder with $a = 5.4308$ Å; computer-controlled microdensitometer [5]). The patterns showed the presence of a new quaternary hydride phase having cubic symmetry and refined cell parameters as stated in the abstract. Intensity calculations suggested that its metal atom arrangement was isostructural to that of Ca$_4$Mg$_4$Fe$_3$H$_{22}$ [1].

A single crystal of Ca$_4$Mg$_4$Co$_3$H$_{19}$ having cubic shape $(0.12 \times 0.12 \times 0.12$ mm$^3)$ was mounted on a Philips PW1100 automatic four-circle diffractometer (Mo Kα radiation, graphite monochromator, absorption coefficient $\mu R = 0.26$). Its cell parameter as refined from 28 measured diffraction angles $(a = 6.7021(5)$ Å), was slightly bigger than that obtained from Guinier data $(a = 6.6953(2)$ Å) and considered to be less reliable. A total of 2667 reflection intensities were collected out to $(\sin\theta/\lambda) = 0.807$ Å^{-1} $(-11 < h < 11, -11 < k < 11, 0 < l < 11)$ in the ω-2θ scan mode, yielding 175 unique reflection intensities with an internal consistency factor of $R_{int} = 4.2\%$. The metal atoms were placed on positions corresponding to those in Ca$_4$Mg$_4$Fe$_3$H$_{22}$ (space group: P$\bar{4}$3m), and the hydrogen sites were located on difference Fourier maps as shown in Fig. 1. The peak heights of the ordered equatorial (H1) and disordered apical (H2) Co ligand sites were $+0.81$ and $+0.46$ eÅ^{-3}, respectively, whereas that of hydrogen not bonded to Co (H3) was $+0.83$ eÅ^{-3}. The structure refinements including atomic position parameters of hydrogen as performed by the XTAL 3.2 system [6] converged at the residuals
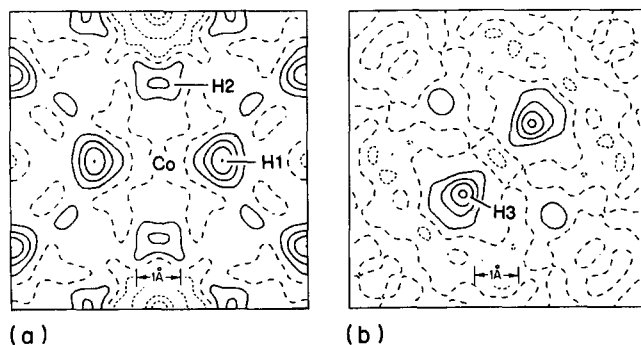
$R(F) = 1.6\%$ and $wR = 1.5\%$ (23 variables, 5 atomic parameters, 6 isotropic Bs, 166 reflections).

Accurate metal–hydrogen bond lengths were obtained from neutron powder diffraction data on the deuteride as collected on the DMC diffractometer [7] at the reactor SAPHIR at PSI, Villigen (Ge(311); $\lambda = 1.7037$ Å, angular 2θ range 3.0–135.0°, 2θ step 0.1°, $T = 295$ K). Each sample (about 4 g) was enclosed in a cylindrical vanadium container of 8 mm inner diameter and measured in the high-intensity mode for 80 min. The transmission factors were measured ($\mu R = 0.236$ for the Ca compound and 0.289 for the Yb compound) and the data corrected accordingly. The profile refinements were performed by using DBWS-9006 [8] and by taking into account the contribution of the impurity phases LiD (Ca and Yb compounds) with NaCl type structure and YbD$_{2.6}$ [9] (Yb compound) with CeD$_{-3}$ like structure [10]. The nuclear scattering lengths (fm), 6.671 (D), -1.90 (Li), 5.375 (Mg), 4.70 (Ca), 2.49 (Co) and 12.43 (Yb), were taken from [11]. The refinements confirmed that the occupancy factors of the equatorial Co ligands D1 and

Table 1
Refinement results on neutron powder and X-ray single crystal (second line) diffraction data ($T = 295$ k)

	Ca$_4$Mg$_4$Co$_3$D$_{19}$	Yb$_4$Mg$_4$Co$_3$D$_{19}$
Space group	P$\bar{4}$3m	P$\bar{4}$3m
a (Å)	6.6809(2)	6.6591(1)
	6.7021(5)	
Ca, Yb in 4(e): x, x, x, etc.	0.7042(7)	0.7042(3)
	0.70402(8)	
U_{iso}(Å$^2 \times 100$)	0.6(2)	0.33(7)
	1.09(2)	
Mg in 4(e): x, x, x, etc.	0.1970(7)	0.1949(8)
	0.1987(2)	
U_{iso}(Å$^2 \times 100$)	1.3(2)	1.4(2)
	1.63(2)	
Co in 3(d): $1/2, 0, 0$, etc.		
U_{iso}(Å$^2 \times 100$)	0.5(2)	0.2(3)
	0.92(1)	
D1 in 12(h): $x, 1/2, 0$, etc.	0.2314(5)	0.2322(7)
	0.225(5)	
U_{iso}(Å$^2 \times 100$)	2.89(9)	2.7(1)
	1.9(9)	
D2^a in 6(f); $x, 0, 0$, etc.	0.2626(14)	0.2632(20)
	0.27(2)	
U_{iso}(Å$^2 \times 100$)	3.1(2)	2.9(3)
	5(3)	
D3 in 4(e): x, x, x, etc.	0.3660(6)	0.3635(6)
	0.366(4)	
U_{iso}(Å$^2 \times 100$)	1.7(1)	1.9(1)
	1(1)	
R values: R_B(%)	5.6	5.0
R_p(%)	4.4	4.9
R_{wp}(%)	5.6	6.3

Fig. 1 Electron density difference maps and hydrogen sites in sections: (a) $\Delta\rho(x, y, 0)$, and (b) $\Delta\rho(x, y, 0.366)$ of Ca$_4$Mg$_4$Co$_3$H$_{19}$ $(\sin\theta/\lambda)_{max} = 0.8$ Å^{-1}, contour intervals 0.2 electrons/Å^3, zero contour dashed, negative contours dotted).

^{a} Half occupied position. Form of temperature factor: $T = \exp[-8\pi^2 U_{iso}(\sin \theta/\lambda)^2]$. Estimated standard deviations in parentheses.

Table 2
Selected interatomic distances (Å)

	$Ca_4Mg_4Co_3H_{19}$[a]	$Ca_4Mg_4Co_3D_{19}$	$Yb_4Mg_4Co_3D_{19}$
Co–4D1(H1)	1.51(3)	1.546(3)	1.546(5)
–2D2(H2)[b]	1.54(13)	1.586(9)	1.58(1)
–4Mg	2.761(1)	2.750(5)	2.738(5)
–4Ca,Yb	3.1209(6)	3.110(5)	3.100(2)
Ca,Yb–3D3(H3)	2.36(3)	2.355(6)	2.357(5)
–6D1(H1)	2.456(7)	2.440(5)	2.431(2)
–3D2(H2)[b]	2.811(8)	2.804(5)	2.794(2)
–3Co	3.1209(6)	3.110(5)	3.100(2)
–3Mg	3.441(2)	3.422(7)	3.403(6)
Mg–3D2(H2)[b]	1.94(3)	1.912(5)	1.891(6)
–D3(H3)	1.94(3)	1.956(6)	1.945(7)
–6D1(H1)	2.425(3)	2.426(5)	2.424(5)
–3Co	2.761(1)	2.750(5)	2.738(5)
–3Ca,Yb	3.441(2)	3.422(7)	3.403(6)
D1(H1)–Co	1.51(3)	1.546(3)	1.546(5)
–2Mg	2.425(3)	2.426(5)	2.424(5)
–2Ca,Yb	2.456(7)	2.440(5)	2.431(2)
–2D1(H1)	2.13(3)	2.186(3)	2.187(5)
–2D2(H2)[b]	2.16(10)	2.215(7)	2.21(1)
D2(H2)[b]–Co	1.54(13)	1.586(9)	1.58(1)
–2Mg	1.94(3)	1.912(5)	1.891(6)
–2Ca,Yb	2.811(8)	2.804(5)	2.794(2)
–4D1(H1)	2.16(10)	2.215(7)	2.21(1)
–4D2(H2)[b]	2.56(13)	2.481(9)	2.48(1)
D3(H3)–Mg	1.94(3)	1.956(6)	1.945(7)
–3Ca,Yb	2.36(3)	2.355(6)	2.357(5)
–3D3(H3)	2.54(4)	2.532(6)	2.571(6)

[a] X-ray single crystal data. [b] Half occupied position. Estimated standard deviations in parentheses.
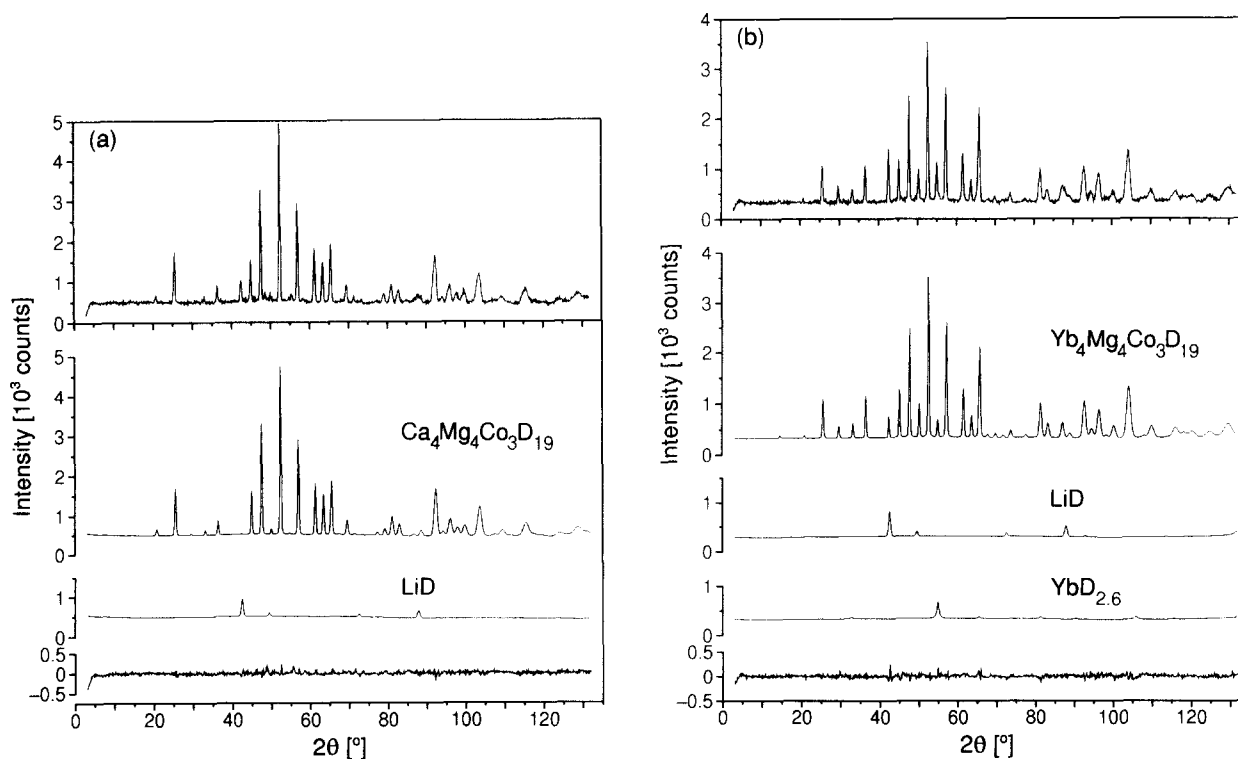

Fig. 2. Observed (top), calculated (middle) and difference (bottom) neutron diffraction patterns of (a) $Ca_4Mg_4Co_3D_{19}$ with the impurity phase LiD, and (b) $Yb_4Mg_4Co_3D_{19}$ with the impurity phases LiD and $YbD_{2.6}$ ($\lambda = 1.7037$ Å).

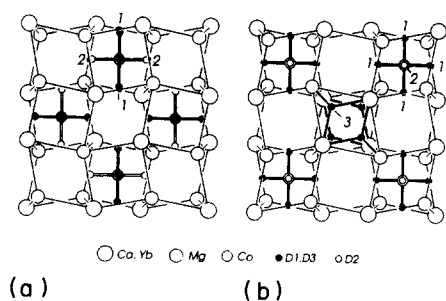O Ca, Yb   O Mg   O Co   ● D1,D3   O D2

(a)   (b)

Fig. 3. Structure slabs of $M_4Mg_4Co_3D_{19}$ (M = Ca, Yb) centred at $z = 0$ (a) and $z = 1/2$ (b), both viewed parallel to the fourfold axes; heavy lines, ordered Co–D bonds; open lines, disordered Co–D bonds; D sites numbered.

Table 3
Co–D bond distances and point group symmetries in square-pyramidal $[CoD_5]^{4-}$ complexes

$Ca_4Mg_4Co_3D_{19}$	$\bar{4}2m(D_{2d})$	1.546(3) Å (4×)	this work
		1.586(9) Å (2×)[a]	
$Yb_4Mg_4Co_3D_{19}$	$\bar{4}2m(D_{2d})$	1.546(5) Å (4×)	this work
		1.58(1) Å (2×)[a]	
Mg_2CoD_5	$4mm(C_{4v})$	1.515(3) Å (4×)	[12]
		1.59(2) Å (1×)	
$Mg_6Co_2D_{11}$[b]	$1(C_1)$	1.53(1) Å (1×)	[13]
		1.55(1) Å (1×)	
		1.56(1) Å (1×)	
		1.57(1) Å (1×)	
		1.62(2) Å (1×)[a]	

[a] Disordered with half occupancy. [b] 1:1 mixture of square-pyramidal $[CoD_5]^{4-}$ and saddle like $[CoD_4]^{5-}$.

the anions D3 did not differ significantly from 100% (D1: 1.00(1), D3: 0.97(2) (Ca); D1: 0.96(2), D3: 0.95(2) (Yb)) whereas that of the disordered apical Co ligand D2 was nearly 50% (D2: 0.53(2) (Ca) and D2: 0.47(2) (Yb)). Therefore, these occupancies were fixed in the final refinement at unity and 0.5, respectively. Results are summarized in Table 1, and interatomic distances and deuterium–deuterium contact distances are given in Table 2. The observed, calculated and difference neutron patterns are shown in Fig. 2, and a structural drawing in Fig. 3.

3. Results and discussion

The structures of $M_4Mg_4Co_3D_{19}$ (M = Ca, Yb) are nearly identical to those of the Fe based analogues $M_4Mg_4Fe_3D_{22}$ [1,2]. Their main difference is the occupancy of the apical transition metal ligand D2, which is half occupied in the Co compounds and fully occupied in the Fe compounds (Fig. 3). This feature is consistent with the presence of orientationally disordered square-pyramidal 18-electron $[CoD_5]^{4-}$ complex anions in the Co compounds, as compared to the ordered octahedral 18-electron $[FeD_6]^{4-}$ anions in the Fe compounds. As expected, the apical bond lengths in the Co compounds [Co–D2] = 1.586(9) Å (Ca) and 1.58(1) Å (Yb) are significantly greater than the equatorial ones [Co–D1] = 1.546(3) Å (Ca) and 1.546(5) Å (Yb), and they do not much differ from the corresponding bond lengths in other $[CoD_5]^{4-}$ containing compounds, such as Mg_2CoD_5 [12] and $Mg_6Co_2D_{11}$ [13] (see Table 3).

The deuteride anions D3 are tetrahedrally coordinated by one Mg at 1.912(5) Å (Ca compound) or 1.902(7) Å (Yb compound), and three Ca at 2.355(6) Å or three Yb at 2.354(5) Å. The corresponding distances in the Fe compounds are [D3–Mg] = 1.808(7) Å (Ca compound) or 1.915(9) Å (Yb compound), and [D3–3Ca] = 2.388(9) Å) [1] or [D3–3Yb] = 2.411(7) Å) [2].

Preliminary experiments suggest that the Ca compound decomposes at 753 K under about 5 bar hydrogen pressure into binary CaH_2 and elemental Co and Mg. In view of its brownish colour in transmitting light the compound is presumably non-metallic. The calculated hydrogen densities are 106 g l^{-1} and 4.2 wt.% for the Ca compound, 107 g l^- and 1.9 wt.% for the Yb compound.

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