



Letter

Structural characterization of $\text{Sr}_4\text{Mg}_4\text{H}_4[\text{CoH}_5]_3$ shows the importance of support from polarizing counter ions to 3d transition metal hydrido complexes



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ABSTRACT

The structure of the title compound was refined from neutron powder diffraction data in the cubic space group $P-43m$ (215). The unit cell contains one formula unit with 3 structurally equivalent $[\text{Co}(\text{I})\text{H}_5]^{4-}$ complexes as well as 4 interstitial hydride (H^-) ions. The presence of the larger and less polarizing Sr^{2+} ions weakens the bond in the complexes and probably also the stability of the structure. Attempts to synthesize the corresponding Ba analogue failed in contrast to using smaller and more polarizing Ca^{2+} and Yb^{2+} counterions.

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1. Introduction

Hydrogen rich transition metal (TM) hydrido complexes can be formed with the help of valence electrons from electropositive alkali and alkali earth metals if they are reacted together in the presence of hydrogen. The bonds in the complexes have a predominantly sd-character, making the 4d- and 5d TM-complexes fairly strong as the soft 4d- and 5d-electrons fit well with the soft and polarisable hydride ligand [1]. There has been a large number of metal hydrides synthesised with such complexes synthesised to date both with alkali and alkaline earth counter ions. There are now several examples such as A_4TMH_6 ($\text{A} = \text{Li, Na, TM} = \text{Ru, Os}$), Ae_2TMH_6 ($\text{Ae} = \text{Mg, Ca, Sr, Ba, TM} = \text{Ru, Os}$), and A_2PdH_2 ($\text{A} = \text{Li, Na}$), K_2PdH_4 [2–5]. Corresponding hydrides based on 3d-electrons are rarer as 3d electrons are harder and have more difficulty to bind with the soft hydride ligand. Most of these hydrides have been synthesised with strongly polarizing Mg^{2+} -ions in the counter ion framework, either alone or in combination with other alkali and alkali earth counterions. This is especially so for the most d-electron rich TMs cobalt and nickel, where no hydrido complex has been synthesised without Mg^{2+} ions in the counterion framework. Here Mg^{2+} has a role beyond a simple counter ion in solid state hydrides, as it helps to relieve some of the electron density via the very polarisable hydride ions, thus strengthening the complexes [1,6]. In solids state hydrides the effect substitute for the

more conventional “back bonding” of electron density to ligand orbitals. In a way this is unfortunate for all the efforts trying to destabilize magnesium hydride (MgH_2) for hydrogen storage by alloying it with nickel, which the well investigated Mg_2NiH_4 system is an example of. Mg_2NiH_4 becomes only marginally less stable than MgH_2 . A possible way to further reduce the stability could be to partially substitute magnesium with a softer and less polarizing counter ion. This gave a less stable hydride in $(\text{NaMgH})_2\text{NiH}_4$ [7]. At present this has little practical implications as the more stable Mg_2NiH_4 phase reforms when $(\text{NaMgH})_2\text{NiH}_4$ was heated to release hydrogen. But if this can be avoided, it might open up for more practical hydrogen storage systems. Another interesting aspect of lattice effects upon this solid state stabilization of d electron rich complexes is that it creates interesting electric conductivity phenomena. Small disturbances in the counter ion lattice have strong impact on the band gaps and the hydrides can switch from conducting to non-conducting by the use of mechanical strain [8,9]. We thus believe that it is interesting to further study how substitution in the counter ion frame works influence the stability of these d electron rich transition metal hydrido complexes. For this we tried to expand the previously discovered $\text{M}_4\text{Mg}_4\text{Co}_3\text{H}_{19}$ ($\text{M} = \text{Ca, Yb}$) series of hydrides featuring the same d^8 electron $[\text{CoH}_5]^{4-}$ complex as in Mg_2CoH_5 [10,11], by exchanging Ca and Yb with the larger and softer alkali earth metals strontium and barium. We can now report how the $[\text{CoH}_5]^{4-}$ complexes changes as a result of the corresponding strontium substitution in $\text{Sr}_4\text{Mg}_4\text{Co}_3\text{H}_{19}$. But interestingly we could not make the corresponding barium analogue.

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2. Experimental details

2.1. Synthesis

All sample handling was performed inside an argon filled glove box with continuously purified atmosphere in order to prevent the reagents and samples from reacting to oxygen and moisture.

SrH₂(D₂) and Mg₂CoH₅(D₅) were prepared in advance by treating lumps of Sr(ABCR 99%) in 30 bar H₂(D₂) at a temperature of 573 K and black colored Mg₂CoH₅(D₅) was made by heat treatment of pelletized MgH₂(D₂) and Co metal powder (Sigma Aldrich 99.8%) in the molar ratio 2:1 under a gas pressure 70 bars at 773 K for 18 h in a corundum crucible inside a stainless steel autoclave. A K-type thermo couple in a steel capillary was attached to the samples for temperature monitoring.

Sr₄Mg₄Co₃H₁₉ was synthesized by mixing powders of SrH₂, Co and Mg₂CoH₅ in the molar ratio 4:1:2. The powders were ground using pestle and mortar, and pelletized. The pellet was put in a corundum crucible and placed in a stainless steel autoclave with attached K-type thermo couple for temperature monitoring. The autoclave was pressurized at 60 bar H₂ gas and heated in a tube furnace to 873 K over night.

The pellet was extracted from the autoclave, crushed and analyzed by powder X-ray powder diffraction to observe eventual impurities. A deuterated sample for neutron diffraction was synthesized the same way by using deuterium.

2.2. X-ray and neutron diffraction

Samples were characterized by X-ray powder diffraction at room temperature using a Panalytical X'pert Pro diffractometer with Cu K α 1 radiation equipped with a Ge[111] monochromator ($\lambda = 1.540598$ Å). The pattern showed the presence of a new quaternary hydride phase having the refined cubic cell parameter $a = 6.9408(1)$ Å. The metal positions were refined using the initial positions of Ca₄Mg₄CoH₁₉. Neutron diffraction was obtained at the TOF instrument GEM at ISIS using a 4 gram sample in a vanadium can Ø = 6 mm sealed by indium wire. The structure refinement was performed in GSAS by least squares Rietveld refinement [12]. Fig. 1 shows a refined neutron diffraction pattern with a difference plot. The initial deuterium structure factors were obtained from Ca₄Mg₄CoD₁₉. The refined unit cell parameter and atomic positional parameters can be found in Tables 1 and 2. As in the earlier published Ca₄Mg₄CoD₁₉ and Yb₄Mg₄CoD₁₉ we could confirm half occupancy for the apical Co–ligand D1, caused by orientational disorder. Interatomic distances and angles are presented and compared to those of Ca₄Mg₄CoD₁₉ and Yb₄Mg₄CoD₁₉ in Table 3.

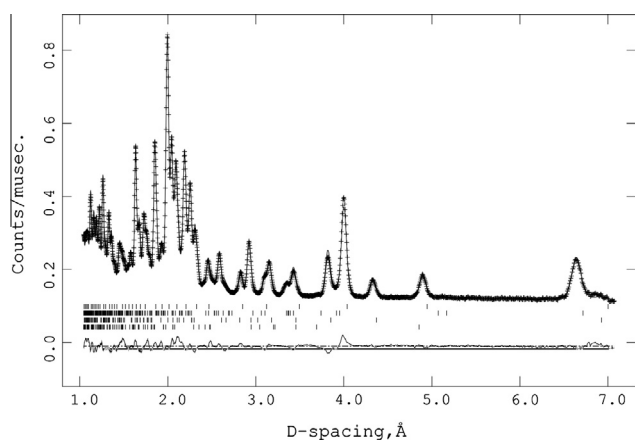


Fig. 1. Observed (crosses) and calculated (line) neutron diffraction intensities and difference plot for Sr₄Mg₄D₄[CoD₅]₃. Tickmarks are from top the main phase, with a refined content of 42 wt%, with impurities SrMg₂CoD₇, 14 wt%, SrMgD₄, 39 wt% and bottom SrD₂, 5 wt%.

Table 1
Refinement parameters for Sr₄Mg₄CoD₁₉.

| |
|--|
| Space group, <i>P</i> -43m (215), <i>Z</i> = 1 |
| <i>a</i> = 6.91372(8) Å |
| <i>R</i> _{wp} (%) = 3.66% |
| Goodness of fit = 6.97 |

Table 2
Atomic parameters for Sr₄Mg₄CoD₁₉.

| Atom | Wyckoff position | Occupancy | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> (Å) ² [2] |
|------|------------------|-----------|-----------|-----------|-----------|-------------------------------|
| Sr | 4e | 1 | 0.7064(4) | 0.7064(4) | 0.7064(4) | 0.0133(9) |
| Co | 3d | 1 | 1/2 | 0 | 0 | 0.009(2) |
| Mg | 4e | 1 | 0.1983(5) | 0.1983(5) | 0.1983(5) | 0.012(1) |
| D1 | 12 h | 1 | 1/2 | 0 | 0.2242(3) | 0.0339(8) |
| D2 | 6f | 0.5 | 0.2684(8) | 0 | 0 | 0.030(2) |
| D3 | 4e | 1 | 0.3544(3) | 0.3544(3) | 0.3544(3) | 0.011(1) |

Table 3
Comparison of interatomic distances and angles for Sr₄Mg₄CoD₁₉ with Ca₄Mg₄CoD₁₉ and Yb₄Mg₄CoD₁₉.

| | Sr ₄ Mg ₄ CoD ₁₉ | Ca ₄ Mg ₄ CoD ₁₉ [10] | Yb ₄ Mg ₄ CoD ₁₉ [10] |
|---------------------|---|--|--|
| Co–D1 × 4 | 1.552(2) | 1.546(3) | 1.546(5) |
| D2 ^a × 2 | 1.621(5) | 1.586(9) | 1.58(1) |
| Mg × 4 | 2.847(4) | 2.750(5) | 2.738(5) |
| Sr × 4 | 3.207(2) | 3.110(5) | 3.100(2) |
| Sr–D3 × 3 | 2.502(3) | 2.355(6) | 2.357(5) |
| D1 × 6 | 2.528(3) | 2.440(5) | 2.431(2) |
| D2 × 3 | 2.880(4) | 2.804(5) | 2.794(2) |
| Co × 3 | 3.207(2) | 3.110(5) | 3.100(2) |
| Mg × 3 | 3.524(4) | 3.422(7) | 3.403(6) |
| Mg–D3 | 1.877(4) | 1.956(6) | 1.945(7) |
| D2 × 3 | 1.991(4) | 1.912(5) | 1.891(6) |
| D1 × 6 | 2.504(4) | 2.426(5) | 2.424(5) |
| D1–Co | 1.552(2) | 1.546(3) | 1.546(5) |
| Mg × 2 | 2.504(4) | 2.426(5) | 2.424(5) |
| Sr × 2 | 2.528(2) | 2.440(5) | 2.424(5) |
| D1 × 2 | 2.195(2) | 2.186(3) | 2.187(5) |
| D2 × 2 | 2.244(4) | 2.215(7) | 2.21(1) |
| D2 ^a –Co | 1.621(5) | 1.586(9) | 1.58(1) |
| Mg × 2 | 1.991(4) | 1.912(5) | 1.891(6) |
| Sr × 2 | 2.880(2) | 2.804(5) | 2.794(2) |
| D1 × 2 | 2.244(4) | 2.215(7) | 2.21(1) |
| D2 × 2 | 2.597(5) | 2.481(9) | 2.48(1) |
| D3–Mg | 1.877(4) | 1.956(6) | 1.945(7) |
| Sr × 3 | 2.502(3) | 2.355(6) | 2.357(5) |
| D3 × 3 | 2.842(3) | 2.532(6) | 2.571(6) |

^a Position is half occupied.

3. Results and discussion

It is interesting to compare the Co–D distances in this work with those in Ca₄Mg₄Co₃D₁₉, Yb₄Mg₄CoD₁₉ and Mg₂CoD₅. The Co–D distances elongate indicating a weaker bond, when substituting magnesium with strontium compared to using ytterbium or calcium or to the corresponding distances in Mg₂CoD₅.

Strontium is larger and less polarizing than both ytterbium and calcium, which both have similar polarizability. In addition to the 15 hydrogen ligands on the three [CoD₅]^{4−} complexes there are 4 interstitial hydride ions (D3) in a tetrahedral site. The apical Co–D2 distance is significantly longer than the Co–D1 distance but it is also significantly longer than the apical Co–D distance in Mg₂CoD₅. The interstitial deuteride anions (D3) are tetrahedral coordinated by 3 Sr atoms and 1 Mg atom with the distances D3–Sr = 2.502(3) Å and D3–Mg = 1.877(4) Å. The D3–Mg distance is significantly shorter than the ones reported in Ca₄Mg₄Co₃D₁₉ and Yb₄Mg₄CoD₁₉, Mg–D = 1.956(6) and 1.945(7) respectively. It is also significant shorter than the Mg–D distance in MgH₂, 1.98 Å. This is probably due to the lower electronegativity of strontium (0.95) compared to calcium (1.0) and ytterbium (1.1). Fig. 2 depicts the [CoD₅]^{4−} complex sitting within a distorted cube with Mg²⁺ and Sr²⁺ ions in alternating corners. The same arrangements can interestingly also be found in the AeMgNiH₄ series (Ae = Mg, Ca, Sr)

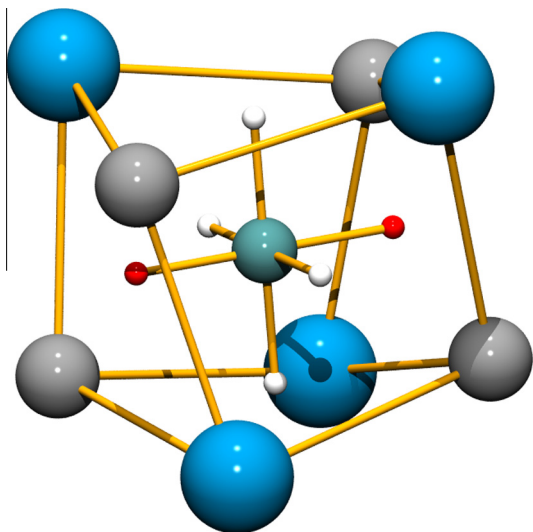


Fig. 2. One of three structural equivalent $[\text{CoD}_5]^{4-}$ complexes in $\text{Sr}_4\text{Mg}_4\text{D}_4[\text{CoD}_5]_3$ within a distorted cube made of alternating Mg^{2+} ions (grey) and Sr^{2+} ions (blue). The complex has a disordered orientation in two directions represented by the red half occupied deuterium position. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

[13]. We also tried to synthesize the corresponding $\text{Ba}_4\text{Mg}_4\text{CoD}_{19}$ but this was not possible, also a corresponding BaMgNiH_4 could not be synthesized as an extension of the AeMgNiH_4 series in spite of significant efforts by the group [13].

This is probably due to an increasing instability in the structures caused by the lesser polarizing support from the counter ion framework, indicating its importance for stabilizing this type of hydrides.

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