

LiSc(BH₄)₄: A Novel Salt of Li⁺ and Discrete Sc(BH₄)₄⁻ Complex Anions

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LiSc(BH₄)₄ has been prepared by ball milling of LiBH₄ and ScCl₃. Vibrational spectroscopy indicates the presence of discrete Sc(BH₄)₄⁻ ions. DFT calculations of this isolated complex ion confirm that it is a stable complex, and the calculated vibrational spectra agree well with the experimental ones. The four BH₄⁻ groups are oriented with a tilted plane of three hydrogen atoms directed to the central Sc ion, resulting in a global 8 + 4 coordination. The crystal structure obtained by high-resolution synchrotron powder diffraction reveals a tetragonal unit cell with $a = 6.076$ Å and $c = 12.034$ Å (space group $P-42c$). The local structure of the Sc(BH₄)₄⁻ complex is refined as a distorted form of the theoretical structure. The Li ions are found to be disordered along the z axis.

Introduction

The development of suitable hydrogen storage materials is a key barrier to the realization of a hydrogen economy. It is currently thought that a viable onboard hydrogen carrier must have very high gravimetric and volumetric hydrogen capacities as well as kinetic and thermodynamic properties that are within rather stringent limits.¹ To date, no directly reversible hydrogen material has been identified that meet all of these criteria. In view of their high theoretical hydrogen storage capacities, metal borohydrides have recently been the subject of intensive investigation.^{2–18} The dehydrogenation of lithium and Group II borohydrides is plagued by severe kinetic limitations and irreversibility that precludes the utilization of these compounds under practical conditions,^{2–10} even as components of binary hydride mixtures.^{12–18} Many transition metal borohydride complexes also have suitable gravimetric hydrogen densities.¹⁹ However, neutral transition metal borohydride complexes, such as Zr(BH₄)₄, can be eliminated a priori from consideration as practical hydrogen carriers because of their high volatility under the conditions required for dehydrogenation.¹⁹ Additionally, the elimination of diborane often competes with dehydrogenation of the neutral complexes.²⁰ In an attempt to circumvent these problems, we have explored the hydrogen storage properties of Group I salts of anionic transition metal borohydride complexes. Preliminary studies have shown these materials to hold promise as practical hydrogen storage materials.²⁰ Efforts to develop these materials would be greatly aided by an understanding of their molecular structure. However, the characterization of this class of complexes has, to date, been limited to ¹¹B NMR spectroscopic studies of LiSc(BH₄)₄.²¹ Thus, structural basics, such as the coordination mode of the [BH₄] ligands, have not been determined. In the present work, we have used a combina-

tion of vibrational spectroscopy, DFT calculations, and X-ray diffraction to elucidate the structure of this new potential hydrogen storage material.

Experimental Details

The compound has been prepared by ball milling of LiBH₄ with ScCl₃ in 4:1 molar ratio.

Raman spectra were obtained by using two different set-ups. The first one is an Ar ion laser (488nm) with a Kaiser Optical Instruments HoloSpec monochromator and a liquid nitrogen cooled CCD camera, and the second is an Ar–Kr laser (568nm) in conjunction with a Spex 1404 double monochromator and a PM detector. The spectral resolution is 3–4 cm⁻¹ for all Raman experiments.

IR spectra were obtained by using a Perkin-Elmer Spectrum One instrument in conjunction with a “Golden Gate” ATR setup. The spectral resolution is 2 cm⁻¹ for the IR experiments.

The samples were handled in a glovebox and were sealed in glass capillaries for the Raman experiments.

The Kohn–Sham²² DFT calculations (PBE²³ exchange–correlation functional and TZP basis set) were applied to optimize the geometry of the studied complexes. For the obtained minima, the vibrational frequencies were calculated in the harmonic approximation. All the computations were performed by using the ADF^{24,25} program package.

Preliminary powder diffraction data (PXD) were measured on the diffractometer STOE IP-PSD equipped with curved image plate detector and using KCu_{α1} radiation. The sample was filled in 1 mm boron-glass spinning capillary. High-resolution synchrotron radiation powder diffraction (SR-PXD) data were collected at the Swiss–Norwegian Beamlines (SNBL, BM01B) at the ESRF, Grenoble, France. A beam with $\lambda = 0.5000$ Å was provided by a double Si monochromator. The angular range $2\theta = 1.00$ – 25.50° was scanned with a detector bank consisting of six scintillation detectors mounted in series with 1.1° separation. The data were binned to the step size $\Delta 2\theta = 0.002^\circ$. The sample was contained in a 0.5 mm boron-glass spinning

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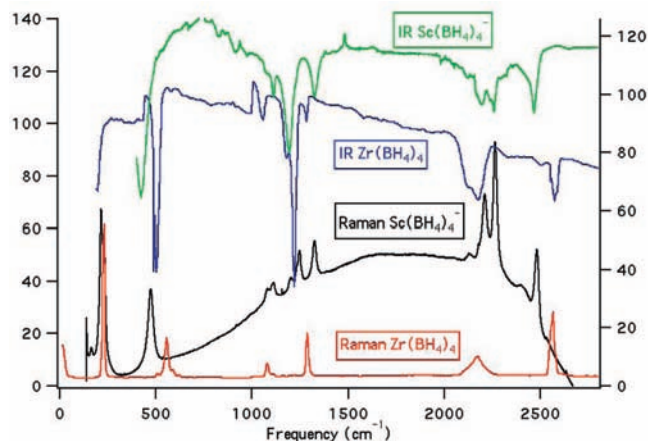


Figure 1. Experimental Raman and IR spectra of $\text{LiSc}(\text{BH}_4)_4$ [this work] and $\text{Zr}(\text{BH}_4)_4$.³³

capillary. The observed reflections of $\text{LiSc}(\text{BH}_4)_4$ were indexed with DICVOL04,²⁶ and the structure was solved with the direct space method program FOX²⁷ and refined with the Rietveld method by using the program TOPAS.²⁸

Results and Discussion

IR spectra of the product confirm that LiBH_4 has completely reacted. This is also supported by the PXD which shows only the presence of LiCl and $\text{LiSc}(\text{BH}_4)_4$ (see below).

As a first structural hypothesis for the new sample (and following the proposal by Nakamori et al.²⁹), the spectra were compared with those reported previously for $\text{Al}(\text{BH}_4)_3$,^{30,31} because one expects from crystallochemical considerations some similarities between Al and Sc. In $\text{Al}(\text{BH}_4)_3$, the central Al has a 6-fold coordination of hydrides in D_3 symmetry.

The literature experimental spectra of $\text{Al}(\text{BH}_4)_3$ present a strong IR band at 1531 cm^{-1} which corresponds to a H–B–H bending mode of E symmetry (labeled ν_{19} in ref 30) of the bridging hydrides.³⁰ This band is not observed in our Sc compound.

A further difference is seen in the Al–B stretching modes. The corresponding strong IR band is observed at 598 cm^{-1} , whereas the strong Raman Al–B band appears at a lower frequency, namely, 495 cm^{-1} . The spectra of the Sc complex, however (see Figure 1), show in this spectral range a strong IR band at a frequency lower than that of the Raman band ($423\text{ vs }474\text{ cm}^{-1}$).

The observation of the highest B–H stretching mode around 2468 (IR) and 2483 (Raman) as well as a doublet around $2200\text{--}2270\text{ cm}^{-1}$ suggests rather the presence of a tridentate B–H binding to the central metal ion.³² The complex $\text{Zr}(\text{BH}_4)_4$ had been shown to present this type of B–H binding, and its vibrational spectra have been published previously.³³ These old data are compared to our new experiments of the scandium complex in Figure 1 and Table 1. Analysis of the results reveals indeed many similarities between both IR and Raman spectra of the two compounds.

We then performed a DFT calculation on the isolated $[\text{Sc}(\text{BH}_4)_4]^-$ complex. The optimization of the geometry without symmetry constraints and the calculation of the vibrational spectra confirm that this ion has a stable structure, similar to the one found for $\text{Zr}(\text{BH}_4)_4$.

The calculated structure (see Figure 2 and Table 2) shows that each BH_4^- ion has a plane of three hydrides oriented partly toward the central Sc atom, resulting in a global $8 + 4$

TABLE 1: Comparison between Experimental IR and Raman Spectra of $\text{LiSc}(\text{BH}_4)_4$ and $\text{Zr}(\text{BH}_4)_4$ ^a

Raman Zr [33]	Raman Sc	Δ	IR Zr [33]	IR Sc	Δ
233	216	17	198		
237	231	6	489	423	66
507			504		
556	474	82	1057	1113	−56
589			1180	1194	−14
	1079		1221		
1080	1112	−32	1284	1325	−41
	1247		2123	2199	−76
1289	1325	−36	2180	2259	−79
2176	2211	−35	2576	2468	108
	2264				
2567	2483	84			

^a All values are in cm^{-1} .

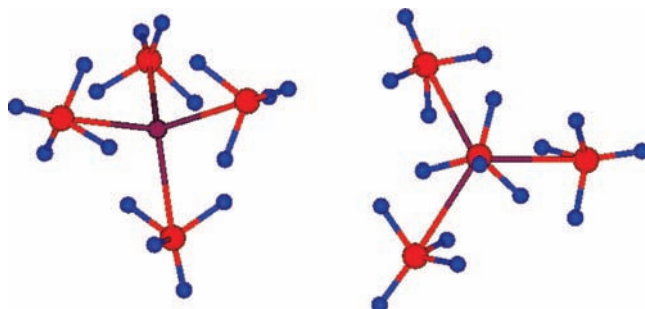


Figure 2. Structure of the $\text{Sc}(\text{BH}_4)_4^-$ complex from the DFT calculations.

TABLE 2: Selected Bond Distances and Angles from the DFT Calculation on the Isolated $\text{Sc}(\text{BH}_4)_4^-$ Ion and as Refined from the Synchrotron PXD^a

	DFT	X-ray
$d(\text{B}-\text{H}_1)$ [Å]	1.21	1.08(2)
$d(\text{B}-\text{H}_2)$ [Å]	1.24	1.08(2)
$d(\text{B}-\text{H}_3)$ [Å]	1.24	1.08(2)
$d(\text{B}-\text{H}_4)$ [Å]	1.24	1.08(2)
$(\text{Sc}-\text{H}-\text{B})_{\text{min}}$ [deg]	75	63
$(\text{Sc}-\text{H}-\text{B})_{\text{max}}$ [deg]	83	95
$d(\text{Sc}-\text{B})_{\text{min}}$ [Å]	2.33	2.28(1)
$d(\text{Sc}-\text{B})_{\text{max}}$ [Å]	2.33	2.28(1)
$(\text{B}-\text{Sc}-\text{B})_{\text{min}}$ [deg]	105	96.5(5)
$(\text{B}-\text{Sc}-\text{B})_{\text{max}}$ [deg]	113	125.4(5)

^a The angles $(\text{Sc}-\text{H}-\text{B})$ are calculated only on the three hydrogen atoms pointing towards scandium.

coordination with 8 Sc–H distances of $2.11\text{--}2.15\text{ Å}$ and 4 Sc–H distances of 2.31 Å . The last B–H bond points to the outside, yielding the high calculated B–H stretching frequencies between 2485 and 2498 cm^{-1} .

Figure 3 compares the calculated and observed IR spectrum.

The calculated frequencies are typically within less than $30\text{--}50\text{ cm}^{-1}$ of the experimental ones. The agreement between those results is surprisingly good when taking into account the three factors influencing the DFT calculations: use of an approximated exchange–correlation functional for the exchange–correlation energy, harmonic approximation, and complete neglect of the effects due to the crystal packing forces.

In view of the previous DFT studies on the alkali borohydrides,³⁴ which showed that the effect of environment on vibrations of the borohydride ion reaches up to 100 cm^{-1} , this overall good agreement is probably the effect of compensation of these three types of errors.

The PXD data showed as a major phase in the sample LiCl ($\sim 60\text{ wt\%}$), and the second phase corresponded to the title

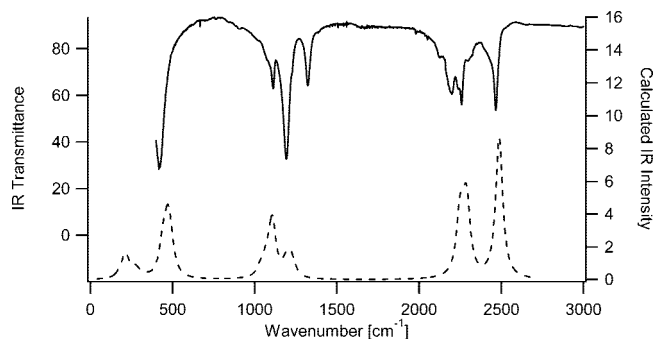


Figure 3. Comparison between observed IR spectrum of $\text{LiSc}(\text{BH}_4)_4$ (full line) and calculated theoretical DFT spectrum (dashed line) for individual $\text{Sc}(\text{BH}_4)_4^-$ ions.

compound. A primitive cubic unit cell ($a = 6.064 \text{ \AA}$) without systematic extinctions explained the positions of the observed reflections of $\text{LiSc}(\text{BH}_4)_4$ in PXD data. The structure was solved in the space group $P23$, providing one Li atom (position $1a$), one Sc atom (position $1b$), and four BH_4 groups (position of the boron atom $4e$) within a unit cell. The structure was solved with the BH_4 groups as rigid bodies with fixed B–H distances of 1.2 \AA .

The high resolution SR-PXD data showed that the symmetry is lower than cubic because some peaks were split. Indexing with the first 20 observed peaks from SR-PXD data showed excellent agreement with a tetragonal unit cell ($a = 6.076 \text{ \AA}$, $c = 12.034 \text{ \AA}$). The observed extinction rules were in agreement with the space groups $P4_2mc$, $P4_2mmc$, and $P-42c$. Because of the good agreement between the PXD data and the cubic structure model, it was assumed that CsCl-type ordering of the Li–Sc sublattice was basically correct. It can be described in any of the three candidate space groups. However, only $P-42c$ has site symmetry for Sc that allows for tetrahedral coordination by four BH_4 tetrahedra. Thus, this space group was assumed as the correct one.

An approximate structure model was obtained by fixing Li and Sc in the positions corresponding to the cubic model (Li on $2e$ and Sc on $2c$), optimizing both the position and orientation of rigid BH_4 tetrahedra. The final Rietveld refinement ($\chi^2 = 1.1$, Rietveld plot in the Supporting Information) of the model showed the disordering of Li around the $2e$ position to the $4k$ position with $z \approx 0.1$ (Table 3 and Figure 4a). The disordering can be understood from the analysis of interatomic distances. The distance between the Li atom and four B atoms from the coordinating BH_4 groups would be 3.00 \AA if Li were on the position $2e$. The disordering of Li to the $4k$ position decreases the number of coordinating BH_4 groups from four to two but with Li–B distances of $2.54(1) \text{ \AA}$ (Figure 4b), closer to this distance observed in LiBH_4 ($2.48\text{--}2.54 \text{ \AA}$).^{3,35} Whether the disordering of Li along the c -axis of the tetragonal structure is of dynamic or static nature stays to be investigated. However, it indicates a high mobility of the Li atoms in this compound which is possibly as good ionic conductor as it was recently recognized for the HT-phase of LiBH_4 .³⁶

As shown in Figure 4, the Sc^{3+} is surrounded by four $[\text{BH}_4]^-$ tetrahedra in deformed tetrahedral coordinations (see table 2 for selected bond distances and angles). A similar tetrahedral coordination of a cation by four $[\text{BH}_4]^-$ anions is known for Li^+ in ambient pressure phases of LiBH_4 ,^{3,35} Zr^{4+} in zirconium borohydride at 113 K ,³⁷ and it was recently observed also for Mg^{2+} in magnesium borohydride.³⁸ As for the Li^+ coordination (discussed above), it looks unusual (Figure 4b) compared to LiBH_4 and reflects the high mobility of the Li^+ cations in the

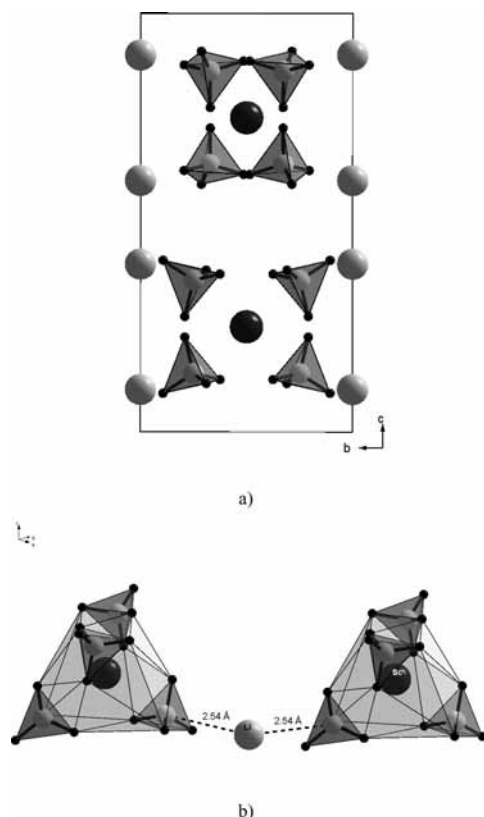


Figure 4. Crystal structure of $\text{LiSc}(\text{BH}_4)_4$ viewed along the a -axis (a) and approximately along the $[1\bar{1}0]$ direction showing the coordination of Li and Sc by BH_4 tetrahedra (b).

structure. On the other side, each $[\text{BH}_4]^-$ is approximately linearly coordinated by one Sc^{3+} and one Li^+ with half-occupancy ($\text{Sc}-\text{B}-\text{Li} = 148.8(5)^\circ$). The coordination of cations by hydrogen atoms cannot be determined unambiguously because of not enough accurate determination of the $[\text{BH}_4]^-$ tetrahedra orientation and Li atom localization. However, from the analysis of the cation coordination in similar borohydrides such as LiBH_4 ,^{3,35} and $\text{Mg}(\text{BH}_4)_2$,³⁸ and from the space filling consideration, we conclude that each Sc^{3+} is coordinated approximately by triangular faces of four BH_4 tetrahedra ($\text{Sc}-\text{H}$ distances $1.92(5)$, $2.08(3)$, and $2.55(8) \text{ \AA}$), thus resulting in an $8 + 4$, relatively irregular hydrogen coordination. The comparison of the DFT structure with the refined crystal structure (see table 2) shows that the distortion from a high symmetry D_3 complex seen by the DFT calculation is pushed further in the crystal structure.

As for Li^+ coordination by hydrogen, it can be understood either by vertices or by edges ($\text{Li}-\text{H}$ distances $1.98(8)$ and $2.5(1) \text{ \AA}$) of two BH_4 tetrahedra. A single B–H distance of $1.08(2) \text{ \AA}$ was refined for rigid BH_4 tetrahedron. It compares well with those in related borohydrides such as LiBH_4 ($1.04\text{--}1.28 \text{ \AA}$).^{3,35}

The Raman spectra suggest that the borohydride groups are not subject to orientation disorder, because the bandwidth remains rather sharp (fwhm ca. 16 cm^{-1} for the B–H bending modes). Raman spectra of the alkali borohydrides have shown significant broadening of the B–H bending modes in the disordered phase.^{39,40}

Finally, we have performed DFT calculations on a model complex comprising two $\text{Sc}(\text{BH}_4)_4$ units separated by four Li atoms to simulate a truncated tetragonal unit cell. Initially, the Li atoms were placed on the $(0\ 0\ 0.6)$ between the two Sc complexes. During the geometry optimization, two diagonally

TABLE 3: Atomic Coordinates of LiSc(BH₄)₄, Symmetry Group *P*-42c, *a* = 6.0759(1), *c* = 12.0338(1) Å

site	x	y	z	B _{iso} [Å ²]	
Li	4k	0	0	0.104(2)	4.0
Sc	2c	1/2	1/2	1/4	3.3(1)
B	8n	0.7500(6)	0.6722(6)	0.6386(3)	1.3(3)
H1	8n	0.7939	0.6688	0.7251	= B _B
H2	8n	0.8960	0.6926	0.5891	= B _B
H3	8n	0.6394	0.8072	0.6234	= B _B
H4	8n	0.6705	0.5201	0.6166	= B _B

^aNote: The displacement parameter of lithium atom refined to very high values and was therefore fixed in the final refinement. The uncertainties of the atomic coordinates for the hydrogen atoms are not reported here, because they were not freely refined. Instead, we report the uncertainty of the rotation parameters (Euler angles) of the BH₄ tetrahedron; they vary between 1.3 and 4.9°.

opposed Li ions moved toward the upper Sc complex, whereas the two others moved to the lower complex in agreement with the preferred Li–B distances of 2.54 Å (Figure 4b).

Although this model calculation is biased by the symmetry constraints and the absence of charge compensation outside of the complex (resulting in several imaginary vibrational frequencies), it confirms the trend of the Li ions to form bonds with the BH₄ units rather than occupy an average central position. The resulting geometry and IR spectra are given in the Supporting Information. Periodic DFT calculations on this compound are planned to account for the effect of the interactions of the studied system with its neighbors present in the solid but absent in the considered theoretical model.

Conclusions

The structure of LiSc(BH₄)₄ has been studied by using a combination of vibrational spectra, DFT calculations, and high-resolution synchrotron powder diffraction. The local symmetry of the isolated Sc(BH₄)₄[−] complex, as obtained from the DFT calculations, was confirmed by the crystal structure analysis. The combined experimental and theoretical results show consistently that each Sc³⁺ is tetrahedrally surrounded by four BH₄[−] tetrahedra with a 8 + 4 coordination of H to Sc. The crystal structure data show in addition disorder for the Li ions, which in turn leads to reasonable Li–B distances. Preliminary DFT calculations on a model complex comprising two Sc(BH₄)₄ units separated by four Li atoms confirm the trend to reduce individual Li–B distances in contrast to the average high-symmetry central position.

The title compound is apparently the same as the material obtained by Nakamori et al. through the balling milling of ScCl₃ and LiBH₄ in 1:3 molar ratio which they misformulated as Sc(BH₄)₃.¹⁸ Their observation of the onset of hydrogen desorption for the compound around 450 K and complete release of hydrogen around 529 K¹⁸ is noteworthy in view of its very high, 14.4, hydrogen weight percentage. Another potential practical application of this material is suggested by our observation of the disordering of Li⁺ in the crystal structure. This finding points to the possibility that this material may be a good conductor of Li ions.

The ionic radius of Al³⁺ is too small to present a similar BH₄[−] coordination, because this would lead to much closer hydride contacts which destabilize the potential [Al(BH₄)₄][−] ion. However, the [Al(BH₄)₄][−] anion is reported to exist.⁴¹ Thus, either the anion is misformulated or the coordinative interactions of the complex ion is very different from those that we have elucidated for LiSc(BH₄)₄.

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Supporting Information Available: Cartesian coordinates of the theoretical model complexes Sc(BH₄)₄[−] and Li₄(Sc(BH₄)₄)²⁺, calculated ADF vibrational frequencies and IR intensities for the isolated complex, calculated IR spectrum of model Li₄(Sc(BH₄)₄)²⁺ complex, and Rietveld plot for synchrotron PXD. The cif file of the structure determination is also included. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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