Metal Tetrahydroborates and Tetrahydroborato Metalates, 17 [1]
Bonding in Cadmium Bis(tetrahydroborate),
and the Reaction with Lithium Tetrahydroborate

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Bonding in Cadmium Bis(tetrahydroborate), Tris(tetrahydroborato)cadmate

Cadmium bis(tetrahydroborate) has been prepared from dimethyl cadmium and H₄B·THF in tetrahydrofuran. Low temperature \(^{113}\text{Cd}\) NMR spectra recorded for THF, monoglyme and diglyme solutions show a septet with \(J(\text{\(^{113}\text{Cd}}\text{H}) = 273\) Hz. This proves that the BH₄⁻ groups are bound to the metal centre via three hydride bridges. Reaction of Cd(BH₄)₂ with LiBH₄ yields LiCd(BH₄)₃ quantitatively in diglyme solution.

The BH₄⁻ group is a very versatile ligand [2]. In mononuclear complexes it can be bound to the metal centre by a single hydride bridge, \(L\text{M} \cdots \text{BH} \cdots \text{H} \text{BH}_2 [3]\), by a double hydride bridge bond, \(L\text{M} \cdots \text{H} \text{BH} \cdots \text{H} \text{BH}_2 [4]\) or by a triple hydride bridge, \(L\text{M} \cdots \text{H} \text{BH}_3 [5]\). It can also act as a bridging group between various metal centres [6, 7]. Reliable information on the bonding can be deduced from vibrational spectroscopy, photoelectron spectroscopy or electron diffraction on well defined species in the gas phase, in a few cases from detailed NMR data using special techniques [7] and of course from X-ray structure determination. However, in solution, where several species are in equilibrium with one another, vibrational spectroscopy is of little value. As shown in previous reports, \(^{113}\text{Cd}\) NMR at low temperature allows the characterization of tetrahydroborato cadmates [1, 8]. We expected that this method might also be useful in determining the still unknown bonding of the BH₄⁻ group in cadmium tetrahydroborate solvates.

Preparation of Cd(BH₄)₂

Cadmium hydroborate was first obtained by the metathesis of CdCl₂ with LiBH₄ in diethyl ether [9]. It was found, however, that it is difficult to obtain chloride free samples owing to the formation of chlorotetrahydroborato cadmates [10]. The reaction between cadmium methoxide and diborane in the presence of either diethyl ether or preferably tetrahydrofuran was suggested as an efficient method for the synthesis of Cd(BH₄)₂ whereas reactions using dimethylcadmium were considered to be less effective [10]. It has now been found that the heterogeneous reaction of H₂B·THF with the insoluble Cd(OMe)₂ in tetrahydrofuran needs a reaction temperature close to -20 °C to enable the process to proceed at an acceptable rate. However, the cadmium tetrahydroborate formed in this reaction begins to decompose at a temperature of about -20 °C [9], more rapidly at -15 °C, to produce a grey metallic precipitate. This decomposition is not quantitative, however, and even after stripping off the solvent an \(^{11}\text{B}\) as well as a \(^{113}\text{Cd}\) NMR spectrum can be recorded at 305 K (\(\delta^{\text{\(^{11}\text{B} \)}} = 49.9\) ppm, \(\delta^{\text{\(^{113}\text{Cd} \)}} = -347\) ppm).

The method found most suitable in the present case is described by equation (1). Removal of all volatile material leads to a solid residue of variable composition Cd(BH₄)n·n THF (n = 2.2–3.7). This material redissolves in THF with only partial decomposition. It also dissolves in a variety of other solvents such as DMF (dimethylformamide), glyme (dimethyl ether of glycol) and diglyme (dimethyl ether of diglycol).

\[
\text{CdMe}_2 + 3 \text{H}_2 \text{B·THF} \rightarrow \text{Cd(BH}_4)_n \cdot n \text{THF} + \text{"BHMe}_2" \cdot (3-n) \text{THF} \tag{1}
\]

The IR spectrum of solid Cd(BH₄)₂·n THF shows a very strong broad band at 2170 cm⁻¹ with a shoulder at 2313 cm⁻¹ and a sharp band of medium intensity at 2427 cm⁻¹ with a shoulder at 2470 cm⁻¹. In addition there is a weaker band at 2401 cm⁻¹.

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cm$^{-1}$. This pattern is reminiscent of vibrational spectra of tetrahydroborates bound to the metal atom via a triple hydride bridge [11]: there should be a band for the terminal BH bond, and two strong bands for the antisymmetric and symmetric vibration of the bridging BH$_3$ group each having a high frequency shoulder due to the presence of the $^{10}$B isotope. The latter are often not very well resolved, giving rise to a single broad and very strong adsorption [12].

**NMR Study of Cd(BH$_4$)$_2$ in Ethereal Solutions**

On the NMR time scale, the BH$_4^-$ group of Cd(BH$_4$)$_2$ is fluxional at ambient temperature. The $^{11}$B NMR spectrum in THF reveals a single quintet ($\delta^{11}$B = −49.1 ppm, $J^{(11)}$B'H$_1$ = 82.0 Hz), demonstrating the magnetic (and chemical) equivalence of all hydrogen atoms. Compared with alkali metal tetrahydroborates [12] ($\delta^{11}$B = −40 to −41 ppm) the boron atoms are better shielded in Cd(BH$_4$)$_2 \cdot n$ THF. On cooling the solution to 213 K, the quintet structure of the $^{11}$B NMR signal is lost. This may be due to rapid quadrupolar relaxation induced by a field gradient [13] which results from static bonding of the BH$_4^-$ group to the cadmium centre. This is ascertained by the low temperature $^{113}$Cd NMR spectrum. The proton decoupled spectrum exhibits only a single, though broad signal, indicating that Cd(BH$_4$)$_2$ in THF solution does not dissociate into ions to any appreciable extent.

![Fig. 1. $^{113}$Cd NMR spectrum of Cd(BH$_4$)$_2$ in THF at 213 K.](image)

There is more information in the undecoupled spectrum shown in Fig. 1 which is a perfect septet ($\delta^{113}$Cd = −346 ppm, $J^{(113)}$Cd'H$_1$ = 273 Hz). Therefore, six equivalent hydrogen atoms are bound to the Cd atom, and this proves the presence of triple hydride bridges, making Cd octacoordinate provided that 2 molecules of THF are bound to the metal atom. The difference of 157 ppm in the $^{113}$Cd chemical shifts of Cd(BH$_4$)$_2 \cdot n$ THF and Cd$_2$·$m$ diglyme [1] is much less than the difference of 281 ppm between the shifts of Cd(BH$_4$)$_3^-$ and Cd$_3^-$, suggesting that the Cd centre in Cd(BH$_4$)$_2 \cdot n$ THF is indeed octacoordinate. In line with this assumption is the broad $^{113}$Cd NMR signal at low temperature which may arise from continued THF exchange even at 213 K. These data therefore suggest structure I for Cd(BH$_4$)$_2 \cdot 2$ THF.

Similar results were obtained for Cd(BH$_4$)$_2$ in monoglyme and diglyme solutions. Solutions were prepared either by dissolving Cd(BH$_4$)$_2 \cdot n$ THF in these solvents or by adding the glymes to THF solutions of Cd(BH$_4$)$_2$ and stripping off all readily volatile materials. In monoglyme solution the $^{11}$B NMR signal is a well-resolved quintet ($\delta^{11}$B = −49.8 ppm, $J^{(11)}$B'H$_1$ = 83.2 Hz). The $^{113}$Cd NMR signal is observed as a single sharp line at $\delta$ = −356 ppm. IR bands in the BH stretching region are observed at 2405 (st), 2193 (m) and 2080 (st) cm$^{-1}$, again indicating triple hydride bridge bonding. The corresponding data for Cd(BH$_4$)$_2$ in diglyme solution are 2399, 2253 and 2187 cm$^{-1}$ ($\nu$BH$_{\text{terminal}}$, $\nu_{\text{asym}}$BH$_3$, $\nu_{\text{sym}}$BH$_3$). The diglyme solution of Cd(BH$_4$)$_2$ exhibits a single $^{11}$B NMR signal at $\delta$ = −50.8 ppm, $J^{(11)}$B'H$_1$ = 83 Hz, and a broad $^{113}$Cd NMR signal at −342 ppm. We have, at the present
time, no explanation for the observation that the 
$^{113}$Cd NMR signal recorded at 305 K is sharp in monoglyme but broad in diglyme. We speculate that the exchange of solvent and BH$_4^-$ may be faster in this solvent than in THF.

On cooling the diglyme solution to 213 K the quintet structure of the $^{11}$B NMR signal collapses and the $^{113}$Cd NMR signal found at $\delta = -333$ ppm is a septet, $\nu(11^3$Cd$^1$H) = 283 Hz. The coupling constant increases, therefore, in the series CdI$_4-n$(BH$_4$)$_2^-$ (157 Hz) through CdI$_3-n$(BH$_4$)$_n^-$ (200 Hz) to Cd(BH$_4$)$_2\cdot n$ solvent (283 Hz); i.e., as one goes from double to triple hydride bridges. Since $\delta(^{113}$Cd) for Cd(BH$_4$)$_2$ changes only little on changing the solvent, we suspect that the average coordination number in ethereal solvents remains constant in all cases.

**Behaviour of Cd(BH$_4$)$_2$ towards Dimethylformamide**

Dissolution of Cd(BH$_4$)$_2\cdot n$ THF in DMF leads to the formation of a metallic precipitate. The $^{11}$B NMR spectrum of the resulting solution is a quintet centred at $\delta^{11}$B = -48.9 ppm, characteristic of BH$_4^-$ attached to a Cd$^{2+}$ ion. In addition there is a quartet at $\delta$ 8.9 ppm, indicating the presence of H$_2$B·NMMe$_3$ [14]. The solution gives also a broad $^{113}$Cd signal at 213 K ($\delta = -391$ ppm), indicative of the presence of Cd(BH$_4$)$_2$. More and more metallic precipitate forms as the solution ages, and after a week only the $^{11}$B quartet signal at $\delta$$^{11}$B = 8.9 ppm remains, together with a very small signal at $\delta$$^{11}$B = -11.6 ppm attributed to minor amounts of H$_2$B·NHMe$_2$ [14]. Thus, Cd(BH$_4$)$_2$ is unstable in DMF solution and reduces this amide to trimethylamine.

**Lithium Tetrahydroborato Cadmate Formation**

As demonstrated in preceding studies [1, 8], the formation of tetrahydroborato cadmates can be monitored at low temperatures using $^{113}$Cd NMR. A fairly complex behaviour has been observed for the metatheses of CdCl$_2$ or CdI$_2$ with alkali metal tetrahydroborates. The interaction of the latter with Cd(BH$_4$)$_2$ should give additional insight into the solution chemistry of Cd(BH$_4$)$_2$. The system LiBH$_4$-Cd(BH$_4$)$_2$-diglyme was used as a model. Since rapid exchange of ligands and coordinated solvent occurs at ambient temperature, only studies at 213/218 K were conducted. The result is shown in Fig. 2.
Addition of LiBH₄ to Cd(BH₄)₂ (1:2 ratio) gives solutions which exhibit two $^{11}$B and two $^{113}$Cd NMR signals, the latter in approximately equal intensity, the former in about a 3:2 ratio. This is in accord with the formation of LiCd(BH₄)₃ as described by equation (2). Under stoichiometric conditions only a single $^{113}$Cd NMR signal at $\delta = -160$ ppm results which is assigned to the Cd(BH₄)₃$^-$ anion [15]. Resolution of the $^{113}$Cd NMR signal in the $^1$H-coupled spectrum is insufficient to extract information on the mode of binding of the BH₄$^-$ group. The signal sharpens somewhat upon proton decoupling, indicating BH₄$^-$ exchange even at this low temperature. This explanation rests also on the fact that additional LiBH₄ [16] influences the line widths of the $^{11}$B and $^{113}$Cd NMR signals (especially the former) whilst having little effect on $^{113}$Cd. We attribute this behaviour to the influence of the Li cation, which is itself a Lewis acid. It interferes with equilibrium (2) making BH₄$^-$ exchange faster then in the presence of a less acidic competitor for BH₄$^-$. 

$$\text{Cd(BH}_4\text{)}_3^- \cdot n \text{d glm} + \text{LiBH}_4 \cdot m \text{d glm} \Leftrightarrow (\text{Li} \cdot m \text{d glm})^+ + \text{Cd(BH}_4\text{)}_3^- + n \text{d glm} \quad (2)$$

**Discussion**

Cadmium bis(tetrahydroborate) is conveniently accessible from diborane and CdMe₂ in THF. However, the THF adduct readily loses coordinated THF, and it is difficult to obtain a well defined solvate such as Cd(BH₄)₂·2THF. In contrast to the cadmium halides, CdCl₂ and CdI₂, no dissociation into solvated cations such as Cd$^{2+}$ and Cd(BH₄)$^+$ and anions Cd(BH₄)₂$^-$ or even Cd(BH₄)₃$^-$ is observed for Cd(BH₄)₂ in THF, monoglyme or diglyme. The compounds Cd(BH₄)₂·n L contain BH₄$^-$ groups bound to the metal centre via a triple hydride bridge. This is in accord with the comparatively large ionic radius of Cd$^{2+}$ and fits with many transition metal tetrahydroborates [7]. Cd(BH₄)₂ is a weaker Lewis acid than the cadmium halides. This is demonstrated not only by the coordination of solvent molecules and the absence of dissociation but also by the fact that Cd(BH₄)₃$^-$ forms readily but not Cd(BH₄)₂$^-$ [16]. In contrast, the ions CdX₃$^-$ and CdX₄$^-$ are both readily accessible.

On the other hand, Cd(BH₄)₂ reduces DMF fairly easily while the anions Cd₁₃₋₄(BH₄)₆$^-$ and CdI₃₋₄(BH₄)₆$^-$ form comparatively stable solutions in this solvent. This reduced activity of the tetrahydroborate cadmates is probably associated with the mechanism of the reduction of DMF. Obviously, DMF will displace ether solvent from Cd(BH₄)₂ before reduction sets in, while BH₄$^-$ or a halide ion is less readily replaced by DMF from the complex ions. The interaction of the cation with DMF plays an essential part in the reduction of the amides as demonstrated by LiBH₄, which reduces DMF fairly fast in contrast to NaBH₄.

**Experimental Part**

All experiments were conducted under dinitrogen gas. Anhydrous solvents were used throughout. CdCl₂ [17] and CdMe₂ [18] were prepared according to literature procedures. A Bruker AC 200 instrument was used for the recording of NMR spectra; conditions for obtaining $^{113}$Cd NMR spectra are described in lit. [8]. $\delta$ values refer to CdMe₂ as the standard, negative signs correspond to frequencies smaller than the standard.

Cadmium-bis(tetrahydridoborate)-tetrahydrofuran

To 1 ml of a 1.66 M Cd(CH₃)₂ solution in diethyl ether were added 5 ml of a 1.3 M H₃B·THF solution (6.5 mmol BH₃) in tetrahydrofuran (THF). After the solution had slowly attained ambient temperature, all volatile material was removed in vacuo. Colourless crystals remained which became a powder on prolonged standing under vacuum. It was noted that the condensate always contained a volatile Cd-containing material.

Dissolution of the solid Cd(BH₄)₂·n THF in THF was always accompanied by partial decomposition resulting in the formation of a grey metallic deposit. The solution gave the following NMR data: $\delta^{11}$B = -49.1, quintet, $^{1}J^{(11)}$B(H) = 82.3 Hz; $\delta^{113}$Cd = -346 ppm, septet, $^{1}J^{(113)}$Cd(H) = 273 Hz. IR (of the solid) in the v BH region (cm⁻¹): 2470 (shoulder), 2427 (st), 2401 (m), 2174 (vst).

**Reaction of Cd(BH₄)₂ with dimethylformamide**

Cd(BH₄)₂ in THF was prepared as described. At $-20$ °C 10 ml of dimethylformamide (DMF) were added. This resulted in an immediate precipitation of a grey material. Recording of NMR spectra shortly after preparing this solution gave the following data: $\delta^{11}$B = -48.9 ppm, quintet, $^{1}J^{(11)}$B(H) = 82.5 Hz; at 213 K: $\delta$ = -49.8 ppm; $\delta^{113}$Cd (223
K) = −391 ppm. After the solution was set aside for one week, a 11B NMR signal at δ11B 8.9 ppm, quartet, 1J(11B-H) = 97 Hz, was observed as well as a very weak signal at δ = −11.6 ppm (quartet).

Solution of Cd/(BH₄)₂ in monoglyme

Cd(BH₄)₂ was prepared from 1.66 mmoles of Cd(CH₃)₂ as described, and 20 ml of CH₂OCH₂CH₂OCH₂ were added to the solution. All volatiles were removed under vacuum, and the oily residue of Cd(BH₄)₂ (monoglyme), was dissolved in monoglyme: δ(B) −49.8 ppm, δ₁₁B = 83.2 Hz; δ₁³Cd −359 ppm. All volatiles were removed under vacuum, and the oily residue of Cd(BH₄)₂-(monoglyme)y was dissolved in monoglyme: δ(B) −50.8 ppm, δ₁₁B = 83 Hz; δ₁³Cd −333 ppm, septet, 2J₁₁B₁₁³Cd = 283 Hz. IR (cm⁻¹), BH region: 2399, 2187, 2183, 2187 cm⁻¹.

Preparation was as described for the solution in monoglyme. The diglyme solution of Cd(BH₄)₂ decomposes quickly at −25 °C. δ₁₁B −50.8 ppm; δ₁³Cd −341.8 ppm; at 218 K: δ₁₁B −50.8 ppm; δ₁³Cd −333 ppm, septet, 2J₁₁B₁₁³Cd = 283 Hz. IR (cm⁻¹), BH region: 2399, 2253, 2187 cm⁻¹.

The appropriate proportions of a Cd(BH₄)₂ solution (0.8 M) and a LiBH₄ solution (1.53 M) were mixed at 0 °C. These solutions were kept at −78 °C before NMR spectra were recorded (213 K for ¹³Cd; 218 K for ¹¹B). The results are presented in tabular form.

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[15] This δ value corresponds to the signal assigned to Cd(BH₄)₂⁺, a species found also in CdX₂−NaBH₄ solutions [1].
[16] It should be noted that a precipitate forms when the ratio LiBH₄/Cd(BH₄)₂ exceeds 1:1. This material did not redissolve in THF.

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