PRODUCTION OF MANGANESE BOROHYDRIDE COMPLEXES OF MANGANESE SOLVATED WITH THF, AND THE STRUCTURE OF $Mn(BH_4)_2(THF)_3$

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Of the tetrahydridoborates of the metals of the first transition series, the least studied at the present time are the borohydride complexes of manganese. In the literature it is only mentioned that $Mn(BH_4)_2$ [1] and $(LiBH_4)_x \cdot (MnX_2)_y$ (X = Cl, I; $1 \leq x \leq 3$, $1 \leq y \leq 4$) [2], and $Mn(CO)_5(BH_4)$ [3] solvated with ether have been obtained. The properties of these compounds were not described, and data on the chemical analysis and spectral characteristics were not provided.

We have obtained and characterized using chemical and combined thermal analytical and IR methods the borohydride complexes of Mn solvated with THF. X-ray structural analysis (XSA) of the complex $Mn(BH_4)_2(THF)_3$ (I) has been performed.

EXPERIMENTAL

The synthesis of the Mn borohydride complexes and the preparation of the sample for physicochemical study were performed under dry N_2 or Ar. The THF was distilled before use over $LiAlH_4$, and the benzene was distilled over P_2O_5. The IR spectra were recorded on a UR-20 spectrophotometer over the range 400-4000 cm^{-1}. The samples were prepared in the form of a suspension in vaseline or in the form of a capillary layer between KBr windows. The thermal analysis was performed on an OD-102 derivatograph with a platinum/platinum–rhodium thermocouple. The precision of the temperature determination was ±5°C, the standard was Al_2O_3, the heating rate was 6 deg/min, the sample size was 0.1-0.5 g. The chemical analysis of the substances obtained was performed at the analytical chemistry laboratory of the Institute of New Chemical Problems of the Academy of Sciences of the USSR.

Technical grade $NaBH_4$ was recrystallized from 8% aqueous NaOH and dried under vacuum at 290-450 K [4]. For the synthesis, a product with a content of the major product > 98% as determined by analysis for the active hydrogen was used.

$MnCl_2$ Preparation. A suspension of powdered Mn in abs. ethanol was mixed in a flow of dry HCl until completely dissolved. H_2 was evolved throughout the reaction and a pale yellow viscous solution formed. The solvent was driven off and the residue dried under vacuum as the temperature was gradually raised to 520 K. $MnCl_2$ was obtained in the form of a flesh-colored powder in a practically quantitative yield. Found, %: Mn 43.5; Cl 56.4%. Calculated: Mn 43.7; Cl 56.3%.

Manganese Borohydride Complex Preparation. To 1.1 g of $MnCl_2$ ($8.7 \cdot 10^{-3}$ mole) in 50 ml THF were added 3.3 g $NaBH_4$ ($8.7 \cdot 10^{-2}$ mole; mole ratio of reagents 1:10) and mixed with a magnetic stirrer at ∿20°C for 30 h (until the chlorine was completely removed from the solution). Following this, the reaction mixture was filtered, the solvent driven off under vacuum, and the residue dried under vacuum at ∿20°C. The product obtained was a yellowish solid. Found: Na 6.4; B 9.3; Mn 16.1; H_{hyd} 3.6%. $NaBH_4 \cdot Mn(BH_4)_2 \cdot 3THF$. Calculated: Na 6.8; B 9.6; Mn 16.2; H_{hyd} 3.6%. Yield, 2.5 g (85%). The product obtained was dissolved in 50 ml benzene, the solutions filtered, the solvent driven off from the filtrate, and the residue dried for 2-3 h at 100 Pa and 300-310 K. A yellow oil was obtained. Found: B 9.4; Mn 24.8; H_{hyd} 3.8%. $Mn(BH_4)_2 \cdot 2THF$. Calculated: B 9.4; M_n 24.0; H_{hyd} 3.5%. Yield, 1.2 g (70%).

$Mn(BH_4)_2 \cdot 2THF$ (II) was dissolved in 40 ml THF, the solvent was driven off, and the residue dissolved for 0.5 h at 295 K and 100 Pa. Compound (I) was obtained in the form of a crystalline, flesh-colored substance. The yield was 1.1 g (70%). Found: B 7.3; Mn 18.4;

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TABLE 1. Coordinates (× 10^4, × 10^3 for H)*

Atom	X	Y	Z	Atom	X	Y	Z
Mn	0	3579,1(4)	1/4	C^5	−403(4)	2882(4)	−1113(3)
O^1	0	1820(2)	1/4	C^6	−785(5)	3367(5)	−295(3)
O^2	138(2)	3354(2)	807(2)	B	1930(3)	4418(4)	3398(3)
C^1	948(4)	1138(3)	3065(7)	H^1	112(3)	487(2)	303(2)
C^2	521(6)	55(3)	3013(6)	H^2	177(3)	348(2)	330(3)
C^3	1171(4)	3147(6)	646(4)	H^3	234(2)	469(3)	428(2)
C^4	866(4)	2748(5)	−490(3)	H^4	233(2)	455(3)	277(2)

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*The equivalent isotropic thermal parameters are available from the author.

H_{hyd} 2.7%. Calculated: B 7.3; Mn 18.4; H_{hyd} 2.7%. Monocrystals of (I) were obtained by slowly cooling a THF solution saturated with the substance at 310 K to ∿20°C.

X-ray structural analysis of (I) was performed on the Enraf-Nonius CAD4-LSI11/02PDP11/23 automated diffractometer system (MoK_α radiation, graphite monochromator). In the experiment a fragment of a monocrystal of (I) ∿0.5 × 0.5 × 0.2 mm^3 was used that had been soldered under argon into a piece of thin-walled Pyrex capillary tubing.

The crystals of (I) are monoclinic, with a molecular formula of $C_{12}H_{32}B_2MnO_3$, M = 300.943; a = 12.513(2), b = 12.412(2), c = 12.663(2) Å, β = 114.34(1)°, V = 1792(1) $Å^3$, Z = 4, $d_{calc} = 1.115$ g/cm³, $\mu(MoK_\alpha) = 7.05$ cm^{-1}, space group C2/c. The intensities were measured for 1744 reflections (ω/2θ scan, $2\theta \leq 50°$). After averaging the equivalent reflections ($R_{int} = 0.012$) and rejecting the weak reflections with $I < 3\sigma(I)$, the number of independent observed reflections was 1255. The crystal structure of (I) was deduced assuming that it was isostructural with the previously studied structure of $Mg(BH_4)_2(THF)_3$ [5]. The structure of (I) was refined by using the full-matrix least squares method in the approximation of anisotropic thermal vibrations for nonhydrogen atoms. Using Fourier synthesis all H atoms of the BH_4 group and some of the H atoms of the THF were detected. The THF H atoms were given geometrically, and their least-squares parameters were not refined, but recalculated after each least-squares cycle and refined in the calculation of the structural amplitudes. In the last cycle of the full-matrix least-squares analysis the ratio of the shifts of the refined parameters to their standard deviation $|\Delta|/\sigma < 0.19$. The final values for the parameters of the atoms are given in Table 1.

The final R factors calculated from 1255 reflections with $I \geq 3\sigma(I)$, have the following values: R = 0.044 and $R_w = 0.063$, the goodness of fit S = 1.43. In the final Fourier synthesis, $\Delta\rho < 0.29$ $eÅ^{-3}$. The weighting scheme of the method of least squares, the f-curves and the anomalous-dispersion corrections Δf' and Δf", the programming and the computer used in this x-ray diffraction study are given in [6].

RESULTS AND DISCUSSION

The reaction between the $NaBH_4$ and the $MnCl_2$ proceeds slowly in THF at ∿20°C without the evolution of heat or gas. For complete removal of Cl from the solution, a large excess of $NaBH_4$ is necessary and the reaction mixture must be mixed for a considerable time, whereupon a light yellow solution with a white precipitate is obtained. Driving off the solvent from the filtrate gives a solid having the formula $NaBH_4 \cdot Mn(BH_4)_2 \cdot THF$ (III). Extraction with benzene allows the borohydride complex Mn(II) to be separated from the $NaBH_4$, which is insoluble in benzene. After filtering the benzene solution and driving off the solvent, oily manganese bis(tetrahydrofuranate) borohydride is separated, which reacts with THF to form crystalline bis(tetrahydrofuranate) (I). A third of the solvent molecules are weakly bound to the complex, and on being slightly heated under vacuum (to 300-320 K) the substance is again converted to an oily product with a variable amount of solvated solvent having an overall composition of $Mn(BH_4)_2 \cdot 2THF$.

A combination of thermal analytical methods applied to compound (I) showed that at 340-350 K melting is observed, at 370-390 and at 400-425 K there occurs the stepwise loss of two molecules of the solvating solvent. Above 370 K, the melt begins to turn dark as the Mn borohydride breaks shown, and at 430 K it decomposes rapidly with intense evolution of gas. In the DTA and DTG curves of complex (II), no effects are noted up to 400 K, and above 400 K

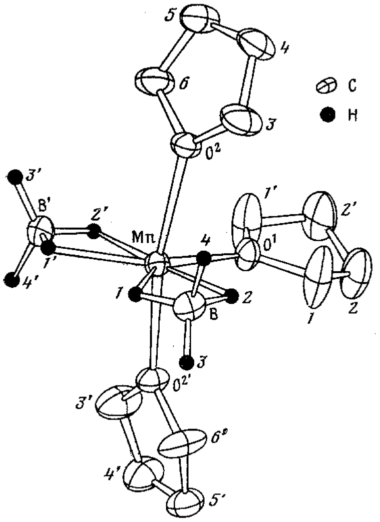
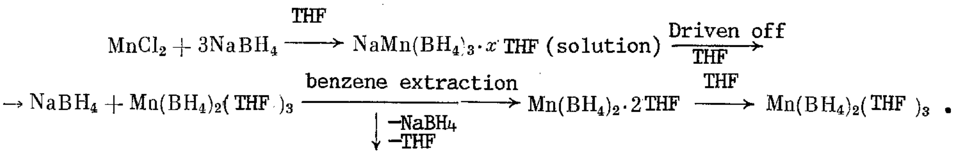


Fig. 1. Structure of $Mn(BH_4)_2(THF)_3$ (I). The atoms of Mn, O, C, and B are presented by probability ellipsoids of thermal vibrations (P = 0.3). $d(BH)_{av}$ = 1.11 Å, major valence angles, in deg: O^1MnO^2 82.82(6), O^1MnB 115.3 (1), O^2MnB 92.7(1), BMnB' 129.5(2), H^1MnH^2 55(1), $H^1MnH^{1'}$ 77 (2), $(O^2MnH)_{av}$ 92.

the thermogram is exactly the same as that of complex (I). The data obtained indicate that it is not possible to completely remove the solvated solvent by heating borohydride complexes (I) and (II) at atmospheric pressure — the removal of the last THF molecule is accompanied by the breakdown of the borohydride complex.

On the thermogram of complex (III) separated from the starting reaction mixture the same thermal effects are noted in the same temperature intervals as for (I). The x-ray diffraction diagram of (III) appears to be the superposition of those of $NaBH_4$ and (I), i.e., the solid product separated from the reaction mixture is not a unique compound, but a mixture of $NaBH_4$ and (I). The stoichiometric ratio of the reagents in the mixture obtained allows one to postulate that during the reaction an anion complex of Mn forms in the solution that decomposes into its original components when the solvent is driven off. The process for obtaining the borohydride Mn complexes can be represented by the following scheme:



$$\mathrm{MnCl_2 + 3NaBH_4 \xrightarrow{THF} NaMn(BH_4)_3\cdot x\,THF\ (solution) \xrightarrow[THF]{Driven\ off}}$$

$$\mathrm{\to NaBH_4 + Mn(BH_4)_2(THF)_3 \xrightarrow[\downarrow\, -NaBH_4,\ -THF]{benzene\ extraction} Mn(BH_4)_2\cdot 2THF \xrightarrow{THF} Mn(BH_4)_2(THF)_3}\ .$$

On the basis of the x-ray diffraction data, the crystal structure of (I) consists of monomers of (I) in which the Mn atom is coordinated with three THF molecules and two bidentate BH_4 groups (Fig. 1). The crystal packing is quite loose, evidence of which is the low value of d_{calc} and the large values of the thermal parameters of the atoms. The molecules of the complex have C_2 symmetry; the second-order axis passes through the atoms Mn and O^1. The Mn coordination polyhedron is a distorted pentagonal bipyramid with the atoms O^2 and $O^{2'}$ at the apices (angle $O^2MnO^{2'}$ = 165.5(1)°), and atoms O^1, H^1, H^2, $H^{1'}$ and $H^{2'}$ (as well as atoms B and B') in the equatorial plane. The conformation of the axial THF rings is an envelope with the angle at atoms O^2 and $O^{2'}$, and the equatorial THF ring lying on the two-fold axis has the half-chair conformation. The interatomic distances and the angles in the THF ligands are close to the expected values. The equatorial distance Mn—O^1 of 2.184(3) is markedly shorter than the axial distance Mn—O^2 of 2.238(2) Å. Compared with $Mg(BH_4)_2(THF)_3$ [5], the Mn—O distance in (I) is increased by 0.1 Å, which increases symbatically with increasing ionic radius of the metal from Mg(II) to Mn(II). The distances Mn...B 2.438(3) and Mn—H 2.04(4) in (I), however, are practically the same as the corresponding bonds in the

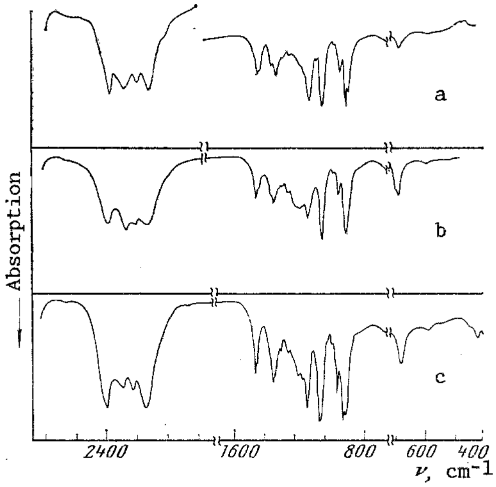


Fig. 2. IR absorption spectra: a) $NaBH_4 \cdot Mn(BH_4)_2 \cdot 3THF$; b) $Mn(BH_4)_2$ 2THF; c) $Mn(BH_4)_2(THF)_3$.

magnesium analog. Taken together, these two facts point to stronger bonding in the BH_4 groups in (I) than in the magnesium complex. On the other hand, the interatomic distances Mn—H and Mn...B in (I) are appreciably longer than in the compounds $Mn(B_3H_8)(CO)_3$ [7], $Mn_2(CO)_6(\mu\text{-}Br)(B_3H_8)$ [8], and $Mn_3(BH_3)_2(H)(CO)_{10}$ [9] containing the bridging bond Mn—H—B, where d(Mn—H) = 1.62-1.69 Å. These facts are evidence of the greater ionicity of the coordination in BH_4 in (I) than in the complexes enumerated above. This conclusion is supported by the IR-spectroscopic data.

Comparing the IR spectra of the compounds obtained by us (Fig. 2) with the IR spectrum of $[Mn(THF)_6](SbCl_6)_2$ [10] we see that in the 400-1300 cm^{-1} region all the absorption bands observed, except the one at 1115 cm^{-1}, correspond to the solvating solvent bound to the metal atom. The band at 1115 cm^{-1} in our opinion, corresponds of the deformational vibration of the BH_4 group, since it is close to the frequency of the deformational vibrations in the IR spectra of complexes of other metals [11].

In the 2000-2500 cm^{-1} region strong bands are observed in the spectra of borohydride complexes that correspond to the stretching vibrations of the B—H bonds. For (I), the strongest bands are at 2390 cm^{-1} (νBH_t) and 2140 cm^{-1} (νBH_b). Between these two bands there are a number of weak bands, most likely the overtones of the deformational vibrations of the BH_2, which are often observed in the IR spectra of other borohydride complexes [12]. The IR spectra of (I) in the 2000-2500 cm^{-1} region differs from typical spectra of borohydride transition metals with BH_4 groups [11], but is similar to the spectrum of the magnesium analog $Mg(BH_4)_2 \cdot (THF)_3$ [5]. In evaluating the ionicity of the bond between the BH_4 and the metal the quantity $\Delta\nu = \nu BH_t - \nu BH_b$. When $\Delta\nu$ = 300-350 cm^{-1} for the covalent borohydrides of the 3d metals, for (I) $\Delta\nu$ = 250 cm^{-1}. The small value of $\Delta\nu$ is evidence of the significant degree of ionicity of the bond between the BH_4 group and the metal. Complex (I) is a more covalent compound than its magnesium analog ($\Delta\nu$ = 150 cm^{-1} [5]). This conclusion is in agreement with the structural data.

The IR spectrum of (II) (cf. Fig. 2) differs from that of (I) by the presence of a strong band at 2285 cm^{-1}, which disappears when THF acts on the complex. Earlier we observed a similar band in the IR spectrum of $Y(BH_4)_3(DME)$, which XSA data indicates is characterized by polymer chains of $[...YH_2BH_2Y...]_n$ [13]. Apparently, on desolvation of (I), the ligands present become insufficient for filling the coordination sphere of the Mn(II), and interaction of manganese ions with BH_4 groups with neighboring molecules leads to the formation of polymer chains. It can be postulated that further removal of the solvating solvent should be accompanied by more extensive polymerization of the Mn borohydride and the completely desolvated $Mn(BH_4)_2$ should have a polymeric (or ionic) structure, be insoluble in nonsolvating solvent, and have a broad absorption band with a maximum near 2290 cm^{-1} in its IR spectrum. The IR spectrum of (III) is the sum of the spectra of sodium borohydride and (I) (cf. Fig. 2).

Comparison of the results we have obtained with data reported in the literature on the borohydride complexes of chromium and iron [11] shows that the borohydride complexes of Mn are significantly more thermally stable and have a more ionic structure that their chromium and iron analogs. It is possible that this is associated with the comparatively stable half-filled d^5-filled shell of the Mn(II) ion.

CONCLUSIONS

By reacting $MnCl_2$ and $NaBH_4$ in THF, the complex $Mn(BH_4)_2(THF)_3$ was obtained and characterized by chemical analysis and physicochemical methods.

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