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Structural and dynamic properties of tetrahydroborate complexes

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Abstract. Data on the structures of tetrahydroborate complexes from X-ray diffraction analysis, neutron and electron diffraction, and IR and NMR spectroscopy are considered. It is shown that, in addition to the diversity of stabilising ligands, complexes of Group III and IV transition metals are characterised by diverse types of coordination of terminal (η^1, η^2 and η^3) or bridging (between neutral molecular units) tetrahydroborate groups. Compounds with BH_4 groups with different denticities can be found among these complexes. Most tetrahydroborates of these metals in the oxidation states +3, +4 comply with the principle of maximum occupancy of the coordination sphere. Tetrahydroborates of Group III and IV metals exhibit clear-cut stereochemical non-rigidity (fluxionality): the protons of the BH_4 ligand are equivalent on the NMR time scale. Group I and V – VIII transition metals mainly form η^2-complexes, which are stereochemically much more rigid than complexes of Group III and IV metals. It is suggested that electronic configuration of the central atom is the crucial factor determining different structures and stereochemical behaviours of the tetrahydroborate complexes. Data on the structures and properties of post-transition and s-element tetrahydroborates are also consistent with this assumption. The bibliography includes 248 references.

I. Introduction

Coordination compounds containing the simplest hydroborate anion BH_4^- as a ligand possess many practically valuable properties. Tetrahydroborate complexes are used as selective reducing agents, starting compounds in the syntheses of complex and organometallic derivatives, precursors for the production of borides, hydrides and other inorganic materials, and as catalysts of hydrogenation, isomerisation, oligomerisation, polymerisation, *etc*. In addition, these complexes exhibit unusual structural and dynamic properties such as the ability to form metal – hydrogen – boron multicentre bonds and exceptionally low barriers to the intramolecular exchange of bridging and terminal hydrogen atoms in the tetrahydroborate ligand.

In mononuclear complexes, a tetrahydroborate ligand either exists as the BH_4^- ion or is linked to the metal through one, two or three M – H – B bridges (η^1, η^2 and η^3 coordination, respectively). The forms of coordination of tetrahydroborate ligands in polynuclear complexes are even more diverse. The BH_4^- anion is isoelectronic with a methane molecule. Therefore, it has been suggested that tetrahydroborates can serve as structural models for some steps in the activation of C – H bonds in saturated hydrocarbons. The existence of complexes with η^1-, η^2- and η^3-BH_4 ligands has been proven by various structural methods. However, the NMR spectra of many tetrahydroborate complexes point to the equivalence of the four protons in the BH_4 group, which indicates that these compounds are fluxional, *i.e*. bridging and terminal protons of the tetrahydroborate ligands are able to undergo fast (on the NMR time scale) intramolecular exchange.[1–5] Thus, most of tetrahydroborate complexes constantly exist in the state of fast dynamic transformation, resulting in the change of the mutual orientation of the complex-forming ion and the tetrahydroborate ligand.

Numerous attempts have been made to explain the unusual properties of tetrahydroborate complexes by such factors as the influence of the Coulomb interaction between the metal ion and the anion, the tendency of the central atom to fill its outer electron shell, the influence of stabilising ligands and so on. A great deal of information on the structures of tetrahydroborates of light elements was provided by *ab initio* quantum-chemical calculations. For transition metal complexes, these calculations are quite cumbersome and have now been performed for only a few objects. It is often impossible to determine unambiguously the most favourable configuration of the complex on the basis of calculations because the energies of different types of coordination of BH_4 ligands differ only slightly; therefore, the results of calculations need to be compared with experimental data (see several papers[6–10] and references therein).

Tetrahydroborate complexes of various metals have been studied to different extents. The structures of tetrahydroborates of Group III and IV transition metals, especially uranium derivatives, and titanium and zirconium compounds have been studied in most detail. Complexes formed by Group I and V – VIII transition metals and by alkali, alkaline earth and post-transition metals are less studied. Therefore, this review starts with a brief characterisation of the physical properties of tetrahydroborate

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complexes and methods for their investigation; the ability of various ligands to stabilise transition metal tetrahydroborates is also considered. This is followed by discussion of the structural and dynamic properties of tetrahydroborates of Group III and IV transition metals with terminal BH_4 ligands and comparison of these properties with the properties of Group I and V–VIII transition metal complexes. An attempt is made to interpret the regularities observed. Data on the structure of alkali, alkaline earth and post-transition metal tetrahydroborates and polynuclear complexes with bridging BH_4 groups are used to verify and refine the correlations found. The results of determination of the structures of tetrahydroborate complexes by electron, X-ray and neutron diffraction analyses and by IR spectroscopy as well as the data on the complexes of Group IV–VIII transition metals, for which the type of coordination of tetrahydroborate ligands has been characterised by NMR spectroscopy, are summarised in tables. Less reliable data on the ligand denticity based only on the results of IR spectroscopy and not confirmed by diffraction methods are cited as little as possible, only where it is necessary to complete the picture.

Hundreds of studies dealing with the investigation or application of tetrahydroborate complexes are published annually. About 200 of these complexes have been structurally characterised; new experimental results have been obtained for them in recent years. However, the questions of what factors determine the structural (type of coordination) and dynamic (stereochemical rigidity or fluxionality) properties of the BH_4 ligands in the complexes and whether or not these properties are related to one another (if they are related, what is the type of relationship) still remain to be answered.

In this review, we analyse the results of experimental determination of the type of coordination of BH_4 groups in different types of complexes by electron, neutron and X-ray diffraction analyses and by NMR spectroscopy. The results are used to make an assumption about the main factors determining the structural and dynamic features of tetrahydroborate complexes.

II. General characteristics of tetrahydroborate complexes

Compounds containing tetrahydroborate ligands are known for all Group IA, IIA and IIIA metals and for all transition metals, except for technetium, promethium, platinum, gold, francium, radium and some actinides, mainly of the berkelium subgroup.[1–5] The results of studies of metal tetrahydroborate complexes by various methods are summarised in Tables 1–3. The formal oxidation numbers of metal atoms in these complexes vary from 0 to +4. Some metals can form the complexes in two different oxidation states [for example, Cu(I) and Cu(II), Yb(II) and Yb(III), U(III) and U(IV), *etc.*]; for titanium, complexes containing the central atoms in four different oxidation states (0, +2, +3, +4) have been structurally characterised. The ion radii of metal cations (r_i) in tetrahydroborates can differ by a factor of more than six [for example, for Be(II), r_i = 0.27 Å, and for Cs(I), r_i = 1.67 Å],[222] the surface area of the coordination sphere can differ by a factor of ~40 and the volume of the central atom, by a factor of 200. The BH_4^- (r_i = 2.04 Å) anion markedly exceeds in size any metal cation which forms complexes with it.[1] Depending on the nature of the central atom, the stabilising ligands and conditions, the compounds in question can be solid, liquid, or gaseous. In the crystalline state, tetrahydroborates having ionic, molecular, islet (ion-molecular) and polymeric (oligomeric) structures are known. Diamagnetic and paramagnetic tetrahydroborate complexes, both low- and high-spin ones, for example (TMEDA)Cr(η^2-BH_4)$_2$ with μ_{ef} = 4.8 μ_B,[93] are known. Some tetrahydroborates are stable in air but most of them are unstable and decompose, often with an explosion, in the presence of air or moisture.

An important characteristic of tetrahydroborate complexes is the manner in which the BH_4 ligand is attached to the central atom. The structures of these complexes are determined most often using X-ray diffraction analysis. In many instances, this method can be used to determine the position of hydrogen atoms and establish the type of ligand coordination. The range of structurally characterised compounds includes complexes with

Table 1. Structurally characterised complexes with terminal BH_4 ligands.

Complex	Distance /Å			Vibration frequencies of the BH_4 group (IR spectroscopy) /cm^{-1}	Ref.
	M–H_b	M···B	B–H_b		
Complexes of Group III and IV transition metals					
Sc(η^2-BH_4)(η^3-BH_4)$_2$(THF)$_2$	2.09(5) m	2.330(5) (η^3) 2.229(5) (η^3) 2.551(5) (η^2)	1.08(5) m	2508, 2420, 2377, 2304, 2242, 2154, 2061, 1348, 1250, 1185, 1124, 1044	11, 12
[(Me$_3$Si)$_2$C$_5$H$_3$]$_2$Sc(η^2-BH_4)	2.03(4)	2.52(2)	1.19(4)	2415, 2125	13
Y(η^2-BH_4)(η^3-BH_4)$_2$(THF)$_3$		2.58 (η^3) 2.68 (η^2)	– –	–	14
Y(η^3-BH_4)$_3$·2 THF				2482, 2300, 2220, 2165, 1250, 1192, 1103, 1042	12, 15
[Y(η^3-BH_4)$_4$]$^-$	–	2.41 m	–		
[Y(η^3-BH_4)$_2$(THF)$_4$]$^+$	–	2.52 m			
(MeOCH$_2$CH$_2$C$_5$H$_4$)$_2$Y(η^2-BH_4)	2.26(5), 2.27(5)	2.773	1.11(5), 1.11(5)	2419, 2367, 2294, 2226, 2197, 2174	16
(EtMe$_4$C$_5$)$_2$Y(η^2-BH_4)(THF)	2.35 m	2.669(4)	–	–	17
La(BH_4)$_3$·3.5 THF				–	18
[La(η^3-BH_4)$_2$(THF)$_5$]$^+$	2.47, 2.59, 2.28	2.730(2)	0.94, 1.15, 1.12	–	
[La(η^2-BH_4)$_2$(η^3-BH_4)$_2$(THF)$_2$]$^-$	2.43, 2.74, 2.55, 2.40, 2.55	2.760(2) (η^3) 2.900(2) (η^2)	0.93, 0.96, 1.49 1.03, 1.13		
(MeOCH$_2$CH$_2$C$_5$H$_4$)$_2$Pr(η^3-BH_4)	–	2.757(18)	–	2404, 2254, 2190	19
(MeOCH$_2$CH$_2$C$_5$H$_4$)$_2$Nd(η^3-BH_4)	–	2.664(25)	–	2404, 2260, 2184	19
(Pr^{i}Me$_4$C$_5$)$_2$Sm(η^3-BH_4)(THF)	2.36(3), 2.51(3), 2.49(3)	2.624(3)	1.18(3), 1.13(3), 1.13(3)	–	20
(MeOCH$_2$CH$_2$C$_5$H$_4$)$_2$Yb(η^2-BH_4)	–	2.800	–	–	19
[Me$_2$Si(3-Me$_3$SiC$_5$H$_3$)$_2$]Yb(η^3-BH_4)(THF)	2.25, 2.22, 2.06	2.470	1.15, 1.20, 1.09	2475, 2385–2240, 2195, 2125	21
Yb(η^3-BH_4)$_2$(MeCN)$_4$	2.46, 2.52, 2.33	2.666(6)	1.19, 1.05, 1.09	2363, 2310, 1604, 1176, 1109	22

Table 1 (continued).

Complex	Distance /Å			Vibration frequencies of the BH_4 group (IR spectroscopy) /cm^{-1}	Ref.
	M − H_b	M···B	B − H_b		
Complexes of Group III and IV transition metals					
Yb(η^3-BH_4)$_2$(Py)$_4$	–	2.692(4)	–	2390, 2360, 2342, 2337, 2248, 2216, 1948, 1876, 1869	22
U(η^2-BH_4)(η^3-BH_4)$_2$(DMPE)$_2$	–	2.84(3) (η^2) 2.68(4) (η^3)	–	2440, 2360, 2340, 2300, 2200, 1125	23
U(η^3-BH_4)$_3$(Ph_2Ppy)$_2$	–	2.61(2) 2.656(8)	–	2420, 2300, 2200, 1120	24
(C_6Me_6)U(η^3-BH_4)$_3$	–	2.54(3) 2.49(4) 2.69(3)	–	2493, 2199, 2122	25
[U(η^3-BH_4)$_3$(DME)(μ-H)]$_2$	–	2.64(4) 2.53(6)	–	2480, 2210, 2140, 1195, 1170, 1095, 1035	26
[Na(THF)$_6$][Cp*U(η^3-BH_4)$_3$]$_2$	–	2.61(2) 2.57(2) 2.68(2) 2.58(2) 2.64(2) 2.59(2)	–	–	27
[U(η^3-BH_4)$_2$(THF)$_5$][(C_7H_7)U$_2$(η^3-BH_4)$_6$]				–	28
[U(η^3-BH_4)$_2$(THF)$_5$]$^+$	–	2.72(4) 2.71(4)	–		
[U(η^3-BH_4)$_3$(C_7H_7)U(η^3-BH_4)$_3$]$^-$	–	2.58(2)	–	–	
[[UCl_5(η^2-BH_4)][U(η^3-BH_4)$_2$(DC18C6)]$_2$				–	29
[UCl_5(η^2-BH_4)]$^{2-}$		2.70(9)	–		
[U(η^3-BH_4)$_2$(DC18C6)]$^+$	–	2.44(12) 2.69(16)	–		
U(η^3-BH_4)$_4$(THF)$_2$	2.16, 2.39, 2.70	2.53(6)	1.15, 1.15, 1.15	–	30
U(η^3-BH_4)$_2$(η^2-BH_4)$_2$(Ph_3PO)$_2$(C_6H_6)	–	2.55(3) (η^3) 2.75(3) (η^2)	–	–	31
U(η^3-BH_4)$_3$(η^2-BH_4)(Ph_3PO)$_2$	2.0, 2.5, 2.8 2.0, 2.5, 2.8 2.0, 2.5, 2.8 2.1	2.51(5) (η^3) 2.58(6) (η^3) 2.65(6) (η^3) 2.84(5) (η^2)	– – –	–	32
Cp U(η^3-BH_4)$_3$	–	2.57(5) 2.46(4)	–	2528, 2156, 2087, 1208	33, 34
Cp_2U(η^3-BH_4)$_2$	–	2.61, 2.58	–	–	35
[1,3-(Me_3Si)$_2C_5H_3$]$_2$U(η^3-BH_4)$_2$	2.42, 2.36, 2.37	2.56(1)	1.13, 1.11, 1.20	2498, 2198, 2120, 1165	36
Cp^*_2U(η^3-BH_4)$_2$	–	2.58(3)	–	–	37
Cp_3U(η^3-BH_4)	–	2.48	–	–	38
(2,4-$Me_2C_5H_5$)U(η^3-BH_4)$_3$	–	2.50(3) 2.52(3) 2.54(3)	–	2518, 2156, 2090	34
(C_4Me_4P)$_2$U(η^3-BH_4)$_2$	2.29(20)	2.553(1)	1.10(15)	–	39
Ind_2U(η^3-BH_4)$_2$	–	2.51(2) 2.53(2)	–	–	40
U(η^3-BH_4)$_3$($OCHPh_2$)(THF)$_2$	–	2.629(7) 2.587(6) 2.599(9)	–	–	41
U(η^3-BH_4)$_2$($OCHPh_2$)$_2$(THF)$_2$	2.527(8), 2.483(9), 2.63(1)	2.711(6)	1.115(8), 1.02(3), 1.03(1)	–	41
(tritox)U(η^3-BH_4)$_3$(THF)	–	2.51(2) 2.65(2)	–	–	42
(tritox)$_3$U(η^3-BH_4)	–	2.58(2)	–	–	42
(COT)U(η^3-BH_4)$_2$($OPPh_3$)	–	2.57(1) 2.66(1)	–	–	43
U{PhC[N($SiMe_3$)$_2$]$_2$}$_2$(η^3-BH_4)$_2$	2.26(3), 2.27(3), 2.31(3)	–	1.08(2), 1.11(3), 1.12(3)	2509, 2209, 2139	44
[($Me_3SiNCH_2CH_2$)$_3$N]U(η^3-BH_4)(THF)	–	2.68(2)	–	2452, 2256, 2201, 2163, 2135, 1246	45
[(Me_3Si)$_2$N]$_3$Th(η^3-BH_4)	–	2.61(3)	–	2500, 2345, 2240, 2180	46
Np(η^3-BH_4)$_4$	2.3(5), 2.1(3), 2.1(3)	2.46(3)	1.0(3), 1.1(2), 1.1(2)	see [a]	47, 48
Ti(η^3-BH_4)$_3$ (see [b])	1.984(5)	2.175(4)	1.276(5)	2585, 2400, 2230, 2155, 2030, 1345, 1265, 1210, 1075, 595, 450	49

Table 1 (continued).

Complex	Distance /Å			Vibration frequencies of the BH_4 group (IR spectroscopy) /cm^{-1}	Ref.
	M – H_b	M···B	B – H_b		
Complexes of Group III and IV transition metals					
$Ti(\eta^2\text{-}BH_4)_3(DME)$	1.93(2), 2.01(2) 1.92(2), 1.87(2) 1.94(2), 1.88(2)	2.424(3) 2.403(2) 2.405(2)	1.22(2), 1.16(2) 1.18(2), 1.16(2) 1.03(2), 1.16(2)	2470, 2420, 2130, 2060	50, 51
$Ti(BH_4)_3(PMe_3)_2$	1.90(6) 1.73(7), 2.25(7), 2.62(7)	2.40(1) 2.27(1)	1.03(7) 0.95(6)	2532, 2401, 2358, 2110	52
$Ti(\eta^2\text{-}BH_4)_2(DMPE)_2$	2.04(2), 2.09(2)	2.534(3)	1.15(2)	2332, 2297, 2220, 2138, 2062	53, 54
$Cp^*Ti(\eta^2\text{-}BH_4)\{(Me_2PCH_2)_3SiBu^t\}$	2.00(5)	2.445(7)	0.98(6), 1.05(5)	–	55
$Cp_2Ti(\eta^2\text{-}BH_4)$	1.75(8)	2.37(1)	1.23(8)	2438, 2400, 2050, 1940, 1315, 1115	56, 57
$Cp_2Ti(\eta^2\text{-}BH_4)$ (see [b])	1.89(5)	2.31(4)	–	–	58
$[CpTi(\eta^3\text{-}BH_4)(\mu\text{-}Cl)]_2$	1.89, 1.90, 2.05	2.17(1)	1.07, 1.18, 1.11	–	59
$\{PhC[N(SiMe_3)]_2\}_2Ti(\eta^2\text{-}BH_4)$	1.92	2.426(4)	1.14	2420, 2395, 2110	60
$[(Me_3Si)_2N]_2Ti(\eta^2\text{-}BH_4)(THF)$	2.08(5), 2.13(5)	2.454(4)	–	2440, 2400, 2270, 2195	61
$[(Me_3Si)_2N]Ti(\eta^2\text{-}BH_4)_2(Py)_2$	1.98(4), 2.03(4) 2.059(4), 1.99(4)	2.476(6) 2.482(5)	–	2380, 2340, 2220, 2140	61
$\{[2,6\text{-}Pr^i_2C_6H_3O]Ti(\eta^3\text{-}BH_4)_2\}_2$	–	2.166(4) 2.162(4)	–	2569, 2560, 2214, 2139, 2097, 2068	62
$[2,6\text{-}Pr^i_2C_6H_3O]Ti(\eta^2\text{-}BH_4)_2(PMe_3)_2$	–	2.457(6) 2.444(6)	–	2412, 2401, 2377, 2368, 2164, 2130	62
$[2,6\text{-}Pr^i_2C_6H_3O]_3Ti(\eta^3\text{-}BH_4)$	–	2.207(13)	–	2528, 2207, 2196, 2140	62
$(Bu^tNCH=CHNBu^t)TiCl(\eta^3\text{-}BH_4)$	1.87(3), 1.90(4), 1.97(3)	2.175(4)	1.12(4), 1.09(4), 1.18(4)	2546, 2173, 2121, 1213	63
$(Bu^tNCH=CHNBu^t)Ti(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)$	1.88(3), 1.87(3) 1.90(3), 1.89(3), 1.91(3)	2.304(3) (η^2) 2.175(3) (η^3)	1.08(3), 1.06(3) 1.02(4), 1.07(3), 1.14(4)	2545, 2178, 2099, 1212	63
$(BP)Ti(\eta^3\text{-}BH_4)_2$	1.978, 1.870, 1.951 1.875, 2.013, 1.984	2.184(7) 2.205(8)	– –	2559, 2542, 2209, 2118	64
$[Ti(CO)_4(\eta^3\text{-}BH_4)]^-[K(18C6)]^+$	2.02(4) m	2.158(7)	1.11(2) m	2495, 2132, 2058	65
$Zr(\eta^3\text{-}BH_4)_4$ (see [b])	2.211(19)	2.308(3)	1.272(16)	–	66
$Zr(\eta^3\text{-}BH_4)_4$	–	2.34(3)	–	2567, 2180, 2115, 1286, 1213, 1170, 1098, 1056, 575, 504	67, 68
$Cp_2Zr(\eta^2\text{-}BH_4)_2$	–	2.59(2)	–	2431, 2375, 2216, 2137, 1294, 1108	69, 70
$[(MeC_5H_4)_2Zr(\eta^2\text{-}BH_4)(THF)][BPh_4]$ (see [c])	1.87(9), 1.93(9) 1.98(9), 1.92(8)	2.54(1) 2.55(1)	1.10(9), 1.30(9) 1.24(8), 1.27(9)	2472 – 2429, 2119	71
$(BP)Zr(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)(THF)$	2.068, 2.036, 2.162 2.125, 1.999	2.354(8) (η^3) 2.572(12) (η^2)	– –	2539, 2458, 2400, 2219, 2117, 2020	64
$Zr(\eta^3\text{-}BH_4)_2\{Me_3SiN[CH_2CH_2N(SiMe_3)]_2\}$	2.04(7), 2.10(5), 2.03(6) 2.21(4), 2.20(8), 2.31(5)	2.370(7) 2.404(7)	– –	2519, 2494, 2236, 2214,2162	72
$Zr(COT)''(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)$	–	2.605 (η^2) 2.368 (η^3)	–	–	73
$Zr_2(COT)''_2(\mu\text{-}H)(\eta^3\text{-}BH_4)$	–	2.33(2)	–	–	73
$Zr(\eta^3\text{-}BH_4)[(3,5\text{-}Me_2Ph)N(Ad)]_3$	2.16(4), 2.21(4), 2.23(4)	2.400(4)	–	2500, 2234, 2180, 2154	74
$Zr_2H_4(\eta^2\text{-}BH_4)_2(PMe_3)_4$	2.16(5), 2.20(5)	2.59(1)	–	–	75
$Zr_3H_6(\eta^2\text{-}BH_4)_2(\eta^3\text{-}BH_4)_4(PMe_3)_4$	2.05(3), 2.11(4), 2.21(3) 2.14(3), 2.15(4) 2.19(3), 2.12(4) 2.08(3), 2.24(3), 2.08(3) 2.06(4), 2.10(4), 2.19(4) 2.35(4), 2.19(3), 2.11(4)	2.352(4) (η^3) 2.610(4) (η^2) 2.655(4) (η^2) 2.363(6) (η^3) 2.361(6) (η^3) 2.394(6) (η^3)	1.17(4), 1.18(4), 1.19(3) 1.14(4), 1.14(4) 1.14(4), 1.13(4) 1.21(4), 1.10(4), 1.14(4) 1.08(4), 1.03(4), 1.19(4) 1.14(4), 1.12(4), 1.14(4)	2530, 2495, 2430, 2400, 2385, 2320, 2230, 2135, 2095	76
$Zr_2H_3(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)_4(PMe_3)_2$	1.98(6), 2.23(7), 2.02(6) 2.05(5), 2.22(6) 2.05(7), 2.17(6), 2.14(5)	2.336(7) (η^3) 2.604(8) (η^2) 2.361(8) (η^3)	1.27(6), 1.05(7), 1.05(6) 1.18(5), 1.03(7) 1.03(8), 1.23(6), 1.01(6)	2550, 2505, 2435, 2390, 2220, 2155, 2102, 1520	77

Table 1 (continued).

Complex	Distance /Å			Vibration frequencies of the BH_4 group (IR spectroscopy) /cm^{-1}	Ref.
	M – H_b	M···B	B – H_b		
Complexes of Group III and IV transition metals					
$Zr_2H_3(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)_4(PMe_3)_2$	2.17(5), 2.04(5), 2.21(5)	2.332(7) (η^3)	1.11(5), 1.19(5), 1.00(5)	2550, 2505, 2435, 2390, 2220, 2155, 2102, 1520	77
	2.14(5), 2.09(6), 2.36(7)	2.357(8) (η^3)	1.07(6), 0.97(6), 1.11(7)		
$Zr_2H_4(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)_3(DMPE)_2$	2.32(8), 2.33(9) 2.08 – 2.47	2.70(1) (η^2) 2.40(2) (η^3)	1.21(10), 1.06(9) 0.94 – 1.38	2490, 2370, 2300, 2200, 2175, 2140	76
$(Bu^tNCH=CHNBu^t)Zr(\eta^3\text{-}BH_4)_2$	2.26(5), 2.03(4), 2.15(5)	2.380(6)	1.16(5), 1.04(4), 1.04(6)	2530, 2216, 2109, 1219, 1208	63
	2.09(5), 2.06(4), 2.30(5)	2.331(5)	1.26(5), 1.11(4), 1.08(5)		
$Zr_3S_3(SBu^t)_2(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)_3(THF)_2$	–	2.53(2) (η^2) 2.33(2) (η^3) 2.35(2) (η^3) 2.35(2) (η^3)	–	–	78
$Zr_6S_6(SBu^t)_4(\eta^2\text{-}BH_4)_2(\eta^3\text{-}BH_4)_6(THF)_2$	–	2.511(11) (η^2) 2.279(2) (η^3) 2.325(11) (η^3) 2.276(12) (η^3)	–	–	78
$Hf(\eta^3\text{-}BH_4)_4$ (see [d])	2.130(9)	2.281(8)	1.235(10)	2570, 2197, 2123, 1290, 1218, 1140, 480	79 – 81
$(MeC_5H_4)_2Hf(\eta^2\text{-}BH_4)_2$ (see [d])	2.069(7), 2.120(8)	2.553(6)	1.255(9), 1.208(13)	2444, 2398, 2235, 2160, 1340, 1120	82
$Hf_2H_3(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)_4(PMe_3)_2$	–	2.33(2) (η^3) 2.53(3) (η^2) 2.34(3) (η^3) 2.35(3) (η^3) 2.32(3) (η^3)	–	2545, 2505, 2430, 2385, 2210, 2160, 2105	77
$Hf_2(NPP)_2H_3(\eta^3,\eta^2,\eta^1\text{-}BH_4)_3$	1.93, 2.43 2.01, 2.25 2.25 m	2.636(7) (η^1) 2.583(6) (η^2) 2.322(8) (η^3)	1.29 m	2520, 2425, 2400, 2144	83
Complexes of Group I and V – VIII transition metals with a bidentate coordination of the BH_4 ligands					
$V(\eta^2\text{-}BH_4)_3(PMe_3)_2$	1.83(3)	2.365(5)	1.14(3)	2431, 2385, 2353, 2227, 2218, 2087	84, 85
$[V(\eta^2\text{-}BH_4)_2(PMe_3)_2]_2O$	1.97(3) m	2.383(6) m	1.15(4) åÆ.	2408, 2397, 2359, 2229, 2106	85
$CpV(\eta^2\text{-}BH_4)(DMPE)$	1.78(4)	2.254(9)	1.17(4), 1.12(8)	2380, 2345, 2255, 1855	86, 87
$[V(\mu\text{-}Cl)(\mu\text{-}DPPM)(\eta^2\text{-}BH_4)]_2$	1.78(8), 1.69(10)	2.314(14)	1.24(9), 1.36(10)	–	88
$[(Me_3Si)_2N]_2V(\eta^2\text{-}BH_4)(THF)$	1.711(7), 1.916(6)	2.38(2)	0.943, 1.43(7)	2434, 2396, 2240, 2134	89
$Cp_2Nb(\eta^2\text{-}BH_4)$	2.0	2.26	1.1	2460, 2423,1745, 1628, 1382, 1162	90, 57
$Me_2C(C_5H_4)_2Nb(\eta^2\text{-}BH_4)$	1.94(7)	2.36(1)	1.25(7)	2461, 2419	91
$Ta_2(\mu\text{-}BH_3)(\mu\text{-}DMPM)(\eta^2\text{-}BH_4)_2(C_7H_8)$	2.16(7), 2.17(7)	2.578(8)	1.09(7), 1.09(7)	–	92
$Ta_2(\mu\text{-}BH_3)(\mu\text{-}DMPM)(\eta^2\text{-}BH_4)_2$	1.82(7), 2.25(8) 2.04(8), 2.12(7)	2.539(10) 2.585(10)	1.13(13), 1.19(7) 1.12(8), 1.16(7)	2376, 2341, 2203, 2122, 2090, 2052	92
$(TMEDA)Cr(\eta^2\text{-}BH_4)_2$	1.931, 2.094 1.875, 2.081	2.44(1) 2.42(1)	– –	2380, 2230, 2120	93
$CrH(\eta^2\text{-}BH_4)(DMPE)_2$	–	2.45	–	2460, 2430, 2060, 1650, 1060, 2330, 2071, 1056	94 54
$Cr(CO)_4(\eta^2\text{-}BH_4)(Ph_3P)_2N$	1.96(7), 1.80(6)	2.29(1)	1.25(8), 1.01(6)	2415, 2365, 2210	95
$Mo(CO)_4(\eta^2\text{-}BH_4)(Ph_3P)_2N$	1.99(9), 2.04(8)	2.413(20)	1.26(11), 1.14(9)	2390, 2375, 2330, 2280	96
$MoH(\eta^2\text{-}BH_4)(PMe_3)_4$	1.96	2.468(12)	1.12	2340, 2290, 1935,1885,1360, 1165	97
$W(\eta^2\text{-}BH_4)(CO)(NO)(PMe_3)_2$	1.8(1), 2.1(1)	2.36(2)	–	2450, 2415	98
$Mn(\eta^2\text{-}BH_4)_2(THF)_3$	2.04(4)	2.438(3)	1.1 m	2390, 2140, 1115	99
$(Ph_4P)[Mn(\eta^2\text{-}BH_4)_3(THF)]$	1.95, 1.98 1.95, 2.18 1.87, 2.24	2.368(3) 2.335(2) 2.362(2)	1.10 m	2395, 2210, 2135, 1110	100, 101
$FeH(\eta^2\text{-}BH_4)[MeC(CH_2PPh_2)_3]$	1.58(11), 1.65(11)	2.16(2)	1.32(12),1.18(10)	2380, 2320, 1910, 1440, 1182	102, 103
$RuH(\eta^2\text{-}BH_4)(PMe_3)_3$	1.81(4), 1.85(4)	–	–	2383, 2369, 2318, 1932	104
$OsH_3(\eta^2\text{-}BH_4)[P(cyclo\text{-}C_5H_9)_3]_2$	1.90	2.30(1)	1.31	2448, 2427, 2130, 2112	105
$Co(\eta^2\text{-}BH_4)(terpy)$	1.81(5), 1.80(5)	–	1.44(6), 1.27(4)	2420, 2403, 2325,2000, 1985, 1927, 1893, 1190	106
$Co(\eta^2\text{-}BH_4)(terpy)$ (see[d])	1.707(12), 1.740(12)	–	1.290(9), 1.287(10)		106
$CoH(\eta^2\text{-}BH_4)[P(cyclo\text{-}C_6H_{11})_3]_2$	1.80(8), 1.87(9)	2.14(1)	1.30(7), 1.39(9)	2390, 2368, 1958, 1379	107, 108
$Co(\eta^2\text{-}BH_4)[MeC(CH_2PPh_2)_3]$	1.55(15), 1.45(15)	2.21(3)	1.27(16), 1.38(17)	2370, 2330, 2015	109

Table 1 (continued).

Complex	Distance /Å			Vibration frequencies of the BH_4 group (IR spectroscopy) /cm^{-1}	Ref.
	M – H_b	M···B	B – H_b		
Complexes of Group I and V – VIII transition metals with a bidentate coordination of the BH_4 ligands					
$Rh_2(\eta^2\text{-}BH_4)_2(\mu\text{-}CO)(Ph_2Ppy)_2$	–	2.29(5) 2.23(5)	–	2421, 2383, 1383, 1138	110
$NiH(\eta^2\text{-}BH_4)[P(cyclo\text{-}C_6H_{11})_3]_2$	1.73(5), 1.76(6)	2.201(8)	1.27(5), 1.30(5)	2360, 2050, 2020, 1868, 1140	111, 112
$Cu(\eta^2\text{-}BH_4)$(dmphen)	1.58(5)	2.08(2)	–	–	113
$Cu(\eta^2\text{-}BH_4)$(dmdphen)	1.50(5)	2.116(12)	–	2385, 2350, 2245, 1982, 1128	114
$Cu(\eta^2\text{-}BH_4)$(phen)(PPh_3) (see[d])	2.03(9), 1.63(7)	2.29(2)	1.24(3), 1.17(3)	2360, 2330, 2245, 2070, 1910, 1120	114
$Cu(\eta^2\text{-}BH_4)$(phen)[$P(OEt)_3$]	2.16(10), 1.98(10)	2.34(1)	0.81(16), 0.83(13)	2360, 2330, 2080	115
$Cu(\eta^2\text{-}BH_4)(PPh_3)_2$	1.82(3)	2.185(6)	1.07(3)	2392, 2350, 2262,1984,1924	3, 116
$Cu(\eta^2\text{-}BH_4)(PBuPh_2)_2$	1.60(10), 1.80(10)	2.20(1)	1.00(10), 1.40(10)	2404, 2394, 1995, 1937, 1139	117, 118
$Cu(\eta^2\text{-}BH_4)$(DPPF)	1.65(6), 1.60(6)	2.158(8)	1.17(7), 1.23(6)	2397, 2354, 2013, 1970	119
$\{CH_2N(CH_2CH_2PPh_2)_2Cu(\eta^2\text{-}BH_4)\}_2$	1.683, 1.681	2.247(6)	–	2365, 2010, 1120	120
Complexes of Group I and V – VIII transition metals with a monodentate coordination of the BH_4 ligand					
$V(\eta^1\text{-}BH_4)_2(DMPE)_2$	1.88	2.833	1.12(3)	2341, 2312, 2110,2095, 1060	54, 84
$Py_4Cr(\eta^1\text{-}BH_4)_2$	1.94 2.33	3.253 3.309	1.16 0.98	2300, 2180, 2120, 2080, 1080 – 1040	93
$FeH(\eta^1\text{-}BH_4)(DMPE)_2$	1.72	2.84	1.14	2350, 2075, 1060	121 – 123
$RuH(\eta^1\text{-}BH_4)\{Me_8[16]aneS_4\}$	1.83	2.895(16)	1.09	2320, 2265, 1055	124
$Cu(\eta^1\text{-}BH_4)(PMePh_2)_3$	1.83(8)	2.578(10)	1.19	2315, 2045, 1060	125, 126
$Cu(\eta^1\text{-}BH_4)(PMePh_2)_3$ (see[d])	1.697(1)	2.518(3)	1.170(5)		125
$Cu(\eta^1\text{-}BH_4)\{MeC(CH_2PPh_2)_3\}$	1.60(4)	2.44(2)	–	2300, 1980	109, 127
$Ag(\eta^1\text{-}BH_4)(PMePh_2)_3$	1.76(7)	2.80(1)	1.2(1)	2300, 2050, 1070	128, 129
$Cu(\eta^1\text{-}BH_4)_2$(Cyclam)	2.28(1)	3.09(1)	0.98(9)	2315, 2227, 2156, 1104	130 – 132
$Cu(\eta^1\text{-}BH_4)_2$(TMAC)	2.25(1)	3.18(1)	1.16(6)	2377, 2333, 2321, 2160, 1118	130 – 132
Complexes of post-transition metals					
$Zn(\eta^2\text{-}BH_4)$(Cl)(TMEDA)	1.983(2), 1.963(2)	2.29(2)	–	2422, 2368, 2207, 2120	133
$(Ph_4P)[Zn(\eta^2\text{-}BH_4)_3]$	1.80	2.22	1.1	2455, 2438, 2410, 2060	134, 135
$V_2Zn_2(\eta^2\text{-}BH_4)_2(PMePh_2)_4$	1.78(5), 1.82(5)	–	–	–	136
$CpNb(CO)(\mu\text{-}H)Zn(\eta^2\text{-}BH_4)_2$	1.839, 1.871 1.736, 1.942	–	0.986, 1.056 1.067, 1.026	2445, 2420, 2100	137
$Cd(\eta^2\text{-}BH_4)[HB(3,5\text{-}Me_2pz)_3]$	–	2.423(5)	–	2426, 2384, 2037	138
$H_2Ga(\eta^2\text{-}BH_4)$ (see[c])	1.826	2.179	1.334	–	139
$HGa(\eta^2\text{-}BH_4)_2$ (see[c])	1.762 – 1.891	2.172	1.250 – 1.456	2566, 2550, 2488, 2478, 2471, 2042, 2026, 1984, 1976, 1971, 1961	140
$Me_2Ga(\eta^2\text{-}BH_4)$ (see[c])	1.791	2.163	1.217	2540, 2470, 1980, 1922	141, 142
$Cp(CO)_2Fe\overline{Ga(\eta^2\text{-}BH_4)(CH_2)_3N}Me_2$	–	2.374(3)	–	2419, 2376	143
$Me_2In(\eta^2\text{-}BH_4)$ (see[e])	–	–	–	–	144
Complexes of s-elements and aluminium					
$Li(\eta^3\text{-}BH_4)[HC(3,5\text{-}Me_2pz)_3]$	–	2.223(7)	–	2374 ,2314, 2223, 2163	145
$[Li(\eta^1\text{-}BH_4)]_2$(18C6)	1.7(2)	2.36(3)	1.1(2)	–	146
$Li(\eta^2\text{-}BH_4)(DME)_2$	1.7(2)	2.470(4)	1.17(2)	2373, 2281, 2258, 2134	147
$\{Li(\eta^2\text{-}BH_4)(TG)\}_\infty$	–	2.478(6)	–	2560, 2382, 2330, 2295, 2264, 2198	147
$Li(\eta^3\text{-}BH_4)(THF)_3$	2.02(4), 2.10(5), 2.12(4)	2.319(7)	1.15(3)	2382, 2334, 2272, 2237, 2176, 2127, 2111	147
$Li(\eta^2\text{-}BH_4)(Py)_3$	2.06, 1.90	2.401(7)	1.15, 1.07	2354, 2309, 2279, 2245	148
$Li(\eta^3\text{-}BH_4)(py^*)_3$	2.07, 2.08, 2.26	2.279(4)	1.15, 1.11, 1.12	2231, 2230, 2209, 2149	148
$Li(\eta^2\text{-}BH_4)(coll)_2$	1.83	2.252(6)	1.17(2)	2421, 2330, 2268	148
$Li(\eta^2\text{-}BH_4)$(PMDETA) (see[c])	2.05(4), 2.04(4) 1.92(4), 1.92(2)	2.29(2) 2.35(2)	1.07(4), 1.07(4) 1.31(4), 1.30(4)	2324, 2284, 2210, 2198, 2181, 2163, 2102	148, 149
$NaBH_4$(15C5)	–	2.70	–	–	150
$CpBe(\eta^2\text{-}BH_4)$ (see[a])	1.78(9)	1.88(1)	1.29(5)	2475, 2424, 2170,1477, 1131, 990, 823	151, 152
$(Bu^tO)_4Be_3(\eta^2\text{-}BH_4)_2$	1.47(8), 1.63(9)	1.93(1)	1.04(7), 0.89(7)	–	153
$Mg(\eta^2\text{-}BH_4)_2(THF)_3$	2.09(4), 1.97(4)	2.451(4)	1.10(4), 1.23(4)	2400, 2370, 2310, 2250, 2090	154
$Ca(\eta^3\text{-}BH_4)_2(DME)_2$	2.474(30), 2.451(29) 2.475(28) 2.345(29), 2.429(31) 2.577(29)	2.646(4) 2.665(5) 	1.121(34), 1.086(34) 1.085(29) 1.135(33), 1.153(29) 1.041(31)	2370, 2350, 2250, 2210, 2160	155
$Ca(\eta^2\text{-}BH_4)_2(\eta^3\text{-}BH_4)$(Diglyme)$_2$ (see[c])	2.41(4), 2.44(3), 2.60(3) 2.32(3), 2.44(3) 2.41(4), 2.47(4), 2.51(4) 2.38(4), 2.41(4)	2.716(4) (η^3) 2.884(4) (η^2) 2.710(4) (η^3) 2.873(5) (η^2)	1.17(4), 1.11(4), 0.91(5) 1.10(3), 1.15(3) 1.05(4), 1.03(4), 1.06(5) 1.04(5), 0.98(4)	–	156

Table 1 (continued).

Complex	Distance /Å			Vibration frequencies of the BH_4 group (IR spectroscopy) /cm^{-1}	Ref.
	M – H_b	M···B	B – H_b		
Complexes of s-elements and aluminium					
$Sr(\eta^3\text{-}BH_4)_2(Diglyme)_2$	2.64(4), 2.65(4), 2.77(4)	2.916(7)	–	2347, 2247, 2167	157
$Sr(\eta^3\text{-}BH_4)_2(18C6)$	2.60(3)	2.833(6)	–	2351, 2297, 2254, 2221, 2164	157
$Ba(\eta^3\text{-}BH_4)_2(Diglyme)_2$	2.69(3), 2.74(4), 2.95(5)	3.058(7)	–	2340, 2274, 2233, 2204, 2153	157
$Ba(\eta^3\text{-}BH_4)_2(18C6)$	2.66(4)	2.975(9)	–	2340, 2285, 2237, 2206, 2154	157
$Al(\eta^2\text{-}BH_4)_3$ (see [b])	1.801(6)	2.143(3)	1.283(12)	2555, 2490, 2218, 2135, 2030, 1930, 1505, 1425, 1112, 605	158 – 160
$Al(\eta^2\text{-}BH_4)_3$					160
α-phase	1.73(4) – 1.76(4)	2.10(2) – 2.14(2)	1.13(4) – 1.14(4)	–	
β-phase	1.67(5) – 1.75(4)	2.10(1) – 2.13(1)	1.12(3) – 1.14(3)	–	
$(PMePh_3)[Al(\eta^2\text{-}BH_4)_4]$	1.77(4), 1.82(4) 1.79(5), 1.80(4) 1.81(5), 1.83(4) 1.77(4), 1.83(5)	2.261(5), 2.229(6) 2.254(7), 2.234(6)	0.95(5), 1.22(5) 1.09(5), 1.15(4) 1.07(4), 1.11(5) 1.04(4), 1.11(5)	2472, 2411, 2240, 2150, 2127	161
$Al(\eta^2\text{-}BH_4)_2Me$ (see [b])	1.82(1)	2.152(16)	1.241	2550, 2485, 2035, 1950, 1496, 1414, 1117, 990	162, 163
$Al(\eta^2\text{-}BH_4)Me_2$ (see [b])	1.77(3)	2.128(8)	1.217(19)	2545, 2475, 2035, 1960, 1540, 1465, 1127, 995	142, 162
$Al(\eta^2\text{-}BH_4)_3(NH_3)$	–	2.229(8)	–	–	164
$Al(\eta^2\text{-}BH_4)_3(NMe_3)$	1.83(7), 1.75(8) 2.00(10), 1.95(11)	2.227(11) 2.257(12)	1.18(7), 1.40(7) 1.16(11), 1.48(10)	2515, 2439, 2150	165, 166
$[Al(\eta^2\text{-}BH_4)_2N(CH_2)_2]_2$	1.65(4), 1.71(4) 1.74(4), 1.84(4)	2.193(5) 2.181(5)	1.26(5), 1.16(5) 1.20(5), 1.22(5)	–	167
$[Al(\eta^2\text{-}BH_4)_2(OSiMe_3)]_2$	–	2.156(5) 2.143(4)	–	–	168

Note. The following designations are used: M – H_b is the distance between metal and bridging hydrogen; DMPE is 1,2-bis(dimethylphosphino)ethane; Ph_2Ppy is 1-diphenylphosphinopyridine; DME is 1,2-dimethoxyethane; Cp* is pentamethylcyclopentadienyl; DC18C6 is dicyclohexyl-18-crown-6; Cp is cyclopentadienyl; Ind is indenyl; tritox is tris(*tert*-butyl)methoxy group, Bu^t_3CO; COT is cyclooctatetraene; BP is methylene-2,2′-bis(4-methyl-6-*tert*-butylphenoxy) group, $CH_2(4\text{-}Me\text{-}6\text{-}Bu^tC_6H_2O)_2$; 18C6 is 18-crown-6; $(COT)''$ is 1,4-bis(trimethylsilyl)cyclooctatetraene; Ad is adamantyl; NPP is bis[dimethyl(dimethylphosphinomethyl)silyl]amide, $N(SiMe_2CH_2PMe_2)_2$; DPPM is bis(diphenylphosphino)methane; DMPM is bis(dimethylphosphino)methane; TMEDA is tetramethylethylenediamine; terpy is 2,2′:6,2″-terpyridyl; dmphen is 2,9-dimethyl-1,10-phenanthroline; dmdphen is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; phen is 1,10-phenanthroline; DPPF is 1,1′-bis(diphenylphosphino)ferrocene; Me_8[16]aneS_4 is 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane; Cyclam is 1,4,8,11-tetraazacyclotetradecane; TMAC is 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane; 3,5-Me_2pz is 3,5-dimethylpyrazolyl; TG is dimethytl ether of triethylene glycol; py* is *p*-benzylpyridine; coll is 2,4,6-trimethylpyridine (collidine); PMDETA is *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine; 15C5 is 15-crown-5; Diglyme is diethylene glycol dimethyl ether.

[a] Neptunium tetrahydroborate is isomorphous with plutonium tetrahydroborate; their IR spectra in the gas phase are similar to the IR spectrum of hafnium tetrahydroborate (see Ref. 48). [b] Gas phase electron diffraction data. [c] Two independent molecules in the crystal cell. [d] Neutron diffraction data. [e] No structural or spectral data were reported.

Table 2. ^{1}H NMR and IR-spectroscopic data for some transition metal tetrahydroborates.

Compound	$\delta(BH_t)$ /ppm	$\delta(MH_xB)$ /ppm	T' /K	T'' /K	$\Delta G^{\neq}$ /kcal mol^{-1}	Vibration frequencies of BH_4 groups (IR spectroscopy) /cm^{-1}	Ref.
$[Ti(CO)_4(\eta^3\text{-}BH_4)]^-[K(18C6)]^+$	0.044	−4.87	178	210	8.8	see [a]	65
$Cp_2V(\eta^2\text{-}BH_4)$	–	−24	–	185	7.6	2442, 2418, 1745, 1650, 1395, 1180	57
$Cp_2Nb(\eta^2\text{-}BH_4)$	5.7	−16.5	–	346	14.6	see [a]	169
$Cp^*_2Nb(\eta^2\text{-}BH_4)$	5.2	−18.2	298	388	16.4	2452, 2428, 1728, 1620, 1171	169
$Ind_2Nb(\eta^2\text{-}BH_4)$	5.7	−14.2	282	331	13.2	2448, 2412, 2311	170
$Cp^*CpTa(\eta^2\text{-}BH_4)$	6.27, 5.91	−15.4	298 [b]	> 323	16.4	2478, 2437, 1747, 1621, 1160	171
$Ta(\eta^2\text{-}BH_4)H_2(PMe_3)_4$	4.39	−4.68	193	–	–	2460, 2440, 1980, 1170	172
$CrH(\eta^2\text{-}BH_4)(DMPE)_2$	−29.4	−33.5	–	–	–	see [a]	94
$[Mo(CO)_4(\eta^2\text{-}BH_4)][(Ph_3P)_2N]$	4.3	−9.8	–	230	10.0	see [a]	96
$MoH(\eta^2\text{-}BH_4)(PMe_3)_4$	5.5	−4.5	193	–	–	see [a]	97
$WH_3(\eta^2\text{-}BH_4)(PMe_3)_3$	−0.13	−6.25	< 273	–	–	2495, 2420, 2060, 1800, 1275, 1140	94
$W(\eta^2\text{-}BH_4)(CO)(NO)(PPh_3)_2$	4.0	−2.7, −1.6	193	–	–	2465, 2425	98
$W(\eta^2\text{-}BH_4)(CO)(NO)[P(OPr^i_3)]_2$	4.61	−3.71, −2.58	193	–	–	2470, 2430	98
$Mn_2(CO)_6(DPPM)(H)BH_4$	2.9	−14.0	243	310	12.2	2472, 2333	173, 174

Table 2 (continued).

Compound	$\delta(BH_t)$ /ppm	$\delta(MH_xB)$ /ppm	T' /K	T'' /K	$\Delta G^{\neq}$ /kcal mol^{-1}	Vibration frequencies of BH_4 groups (IR spectroscopy) /cm^{-1}	Ref.
$Mn_2(CO)_5(DPPM)(H)BH_4$	4.3	−8.6, −12.1 (η^2) −14.6 (η^1)	338 [b]	–	–	2487	174
$Mn_2(CO)_6(TEDIP)(H)BH_4$	–	−15.1	243	–	–	2475, 2360	174
$Mn_2(CO)_5(TEDIP)(H)BH_4$	3.8	−9.5, −12.4 (η^2) −13.45 (η^1)	295 [b]	–	–	2466	174
$Re(\eta^2\text{-}BH_4)(DPPE)_2$	1.27	−9.0	–	–	–	2400, 2330, 1188	175
$ReH(\eta^1\text{-}BH_4)(\eta^2\text{-}BH_4)(PMe_2Ph)_3$	−1.6	−5.3, −13.7	223	–	–	2390, 1100	94
$ReH(\eta^2\text{-}BH_4)(NO)(PPr^i_3)_2$	6.62	−3.91, −6.12	–	–	–	2462, 2437, 1854, 1794	176
$ReH(\eta^2\text{-}BH_4)(NO)[P(cyclo\text{-}C_6H_{11})_3]$	6.62	−3.59, −6.39	–	–	–	2463, 2437, 1843, 1790	176
$ReH(\eta^2\text{-}BH_4)(NO)(PPh_3)_2$	–	−2.92, −4.53	–	–	–	2482, 2446, 1810	176
$FeH(\eta^2\text{-}BH_4)[MeC(CH_2PPh_2)_3]$	–	−14.7	< 253	> 306	–	see [a]	102, 103
$FeH(\eta^1\text{-}BH_4)(DMPE)_2$	0.8	−22.4	197 [b]	~240	–	see [a]	123
$FeH(\eta^1\text{-}BH_4)(DEPE)_2$	–	−21.2	197 [b]	–	–	–	123
$FeH(\eta^1\text{-}BH_4)(DPrPE)_2$	–	−21	197 [b]	–	–	–	123
$Fe_3(CO)_9H(BH_4)$	3.2	−12.8, −15.8	173	–	–	2335	177
$(C_6Me_6)_2Ru_2H_3(BH_4)$	3.2	−13.4	213	–	–	see [a]	178
$CpRu(PPh_3)(\eta^2\text{-}BH_4)$	–	−17.2	–	–	–	2380	179
$Cp^*Ru(PMe_3)(\eta^2\text{-}BH_4)$	2.14, −3.5	−11.05	303	–	–	2438, 2362, 2282	180
$Cp^*Ru(PEt_3)(\eta^2\text{-}BH_4)$	2.10, −3.22	−11.63	303	–	–	2433, 2352, 2284	180
$Cp^*Ru(PPr^i_3)(\eta^2\text{-}BH_4)$	–	−12.54	303	–	–	2393, 2318	180
$Cp^*Ru(PCy_3)(\eta^2\text{-}BH_4)$	–	−12.36	303	–	–	2408, 2329	180
$Cp^*Ru(PPh_2Me)(\eta^2\text{-}BH_4)$	–	−12.0	303	–	–	2387, 2292, 2223	180
$Cp^*Ru(PPh_3)(\eta^2\text{-}BH_4)$	–	−12.03	303	–	–	2450, 2386, 2326	180
$RuH(\eta^2\text{-}BH_4)(PMe_3)_3$	6.1 – 4.5	−6.1 to 79.6	298	< 353	–	2383, 2369, 2318, 1932	104
$RuH(\eta^2\text{-}BH_4)(PMe_2Ph)_3$	5.45	−5.91, −9.08	298	–	–	2402, 2395, 2312	181
$RuH(\eta^2\text{-}BH_4)(PMePh_2)_3$	–	−5.1, −9.1	308	–	–	2395, 2375, 2315, 1945, 1370, 1180	182
$RuH(\eta^2\text{-}BH_4)(PPh_3)_3$	–	−6.87	–	–	–	2382, 2340, 2080, 1119	183
$RuH(\eta^2\text{-}BH_4)[PhP(CH_2)_3PPh_2)_2]$	5.1	−5.8, −7.9	300 [b]	348	–	2390, 2380, 2330, 1180	184
$RuH(\eta^2\text{-}BH_4)[PhP(CH_2)_3PCy_2)_2]$	4.8	−6.8, −9.2	–	–	–	2395, 2330, 1960	185
$RuH(\eta^1\text{-}BH_4)[P(CH_2CH_2PPh_2)_3]$	1.35	−10.28	168	203	–	2360, 2270, 1980, 1052	186
$RuH(\eta^2\text{-}BH_4)(PP_3CyBH_3)$	5.5	−7.0	298	–	–	–	187
$RuH(\eta^2\text{-}BH_4)(CO)(PPr^i_3)_2$	4.55	−4.90, −7.78	233	> 243	–	2420, 2320	188
$RuH(\eta^2\text{-}BH_4)(CO)(PMeBu^t_2)_2$	4.70	−4.40, −7.20	233	> 243	–	2400, 2390	188
$[RuH(CO)(PPr^i_3)_2]_2(BH_4)(BF_4)$		−2.85 (2H) −5.76 (2H)	223	> 243	–	–	189
$RuH(\eta^1\text{-}BH_4)(PNP)(PPh_3)$	2.5	−8.9	193	–	–	2360, 2322, 1915, 1845, 1058	190
$RuH(\eta^2\text{-}BH_4)(S\text{-biphemp})(PPh_3)$	5.8	−4.0, −9.1	293	373	–	2403, 2380, 2333, 1966, 1331,1178	191
$OsH_3(\eta^2\text{-}BH_4)(PPr^i_3)_2$	8.78	−6.78	213	300(H_b-OsH), > 360(H_b-H_t)	13.2	2447, 2351	10, 192
	8.79	−10.14	360		> 20		
$OsH_3(\eta^2\text{-}BH_4)[P(cyclo\text{-}C_5H_9)_3]_2$	9.05	−6.83	193	–	–	see [a]	105
	8.8	−10.19 [b]	363				
$OsH(\eta^2\text{-}BH_4)(CO)(PPr^i_3)_2$	6.10	−6.50, −8.10	233	> 243	–	2430, 2330	188
$OsH(\eta^2\text{-}BH_4)(CO)(PMeBu^t_2)_2$	6.35	−6.15, −7.75	233	> 243	–	2440, 2420	188
$[OsH(CO)(PPr^i_3)_2]_2(BH_4)(BF_4)$		−3.82 (2H) −5.39 (2H)	223	> 243	–	–	189
$Co(\eta^2\text{-}BH_4)terpy$	1.73	−9.97	213	> 254	11.1	see [a]	193
$Rh(\eta^2\text{-}BH_4)H_2(PMeBu^t_2)_2$	3.9	−4.53	300	–	–	–	194
$Ir(\eta^2\text{-}BH_4)H_2(P\ MeBu^t_2)_2$	6.86	−6.86	300 [b]	> 300	–	2458, 2347, 2150, 1308, 1188	195
$Ir(\eta^2\text{-}BH_4)H_2(PBu^t_3)_2$	6.17	−7.76	300 [b]	> 300	–	2460, 2367, 2142, 1330, 1196	195
$Cp^*_2Ir_2H_3(BH_4)$	5.5	−14.2	298	–	–	see [a]	196

Note. The following designations are used: $\delta(BH_t)$ and $\delta(MH_xB)$ refer to the signals of the terminal and bridging hydrogen atoms of the tetrahydroborate ligands, respectively; T' is the temperature at which the spectrum was recorded; T'' is the temperature of coalescence of signals of bridging and terminal protons; $\Delta G^{\neq}$ is the activation energy for the exchange of bridging and terminal protons; TEDIP is tetraethyl pyrophosphite; DPPE is 1,2-bis(diphenylphosphino)ethane; DEPE is 1,2-bis(diethylphosphino)ethane; DPrPE is 1,2-bis(dipropylphosphino)ethane; PP_3Cy is tris(dicyclohexylphosphinoethyl)phosphine, $P[CH_2CH_2P(cyclo\text{-}C_6H_{11})_2]_3$; PNP is 1,2-bis[*N*,*N*-bis(2-diphenylphosphinoethyl)amino]ethane; *S*-biphemp is (*S*)-2,2′-dimethyl-6,6′-bis(diphenylphosphino)biphenyl.

[a] The data of IR spectroscopy are presented in Table 1. [b] The spectrum was recorded under the $^1H-\{^{11}B\}$ double resonance conditions.

mono-, bi- and tridentate terminal BH_4 groups (Fig. 1) and polynuclear complexes with diverse tetrahydroborate bridges between metal atoms (Fig. 2).

If the positions of hydrogen atoms cannot be determined by X-ray diffraction analysis, the denticity of the BH_4 ligand can be estimated from the metal – boron distance. These distances in

Table 3. Polynuclear complexes with bridging tetrahydroborate groups.

Compound	Type of coordination of the BH_4 group according to X-ray diffraction data	See Fig. 2	Vibration frequencies of the BH_4 groups (IR spectroscopy) /cm^{-1}	Ref.
$LiBH_4(Et_2O)$	$\{(Et_2O)Li[(\mu_2\text{-}H)(\mu_2'\text{-}H)(\mu_2''\text{-}H)(\mu_4\text{-}H)B]\}_\infty$	*c*	2364, 2286, 2234, 2230	147, 197
$LiBH_4(MeOBu^t)$	$\{(MeOBu^t)Li[(\mu_2\text{-}H)(\mu_2'\text{-}H)(\mu_3\text{-}H)(\mu_3'\text{-}H)B]\}_\infty$	*d*	2410, 2320, 2306, 2277, 2180	147
$LiBH_4(C_3H_6O_2)$	$\{(C_3H_6O_2)Li[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)_2B]\}_\infty$	*a*	2317, 2256, 2180	147
$LiBH_4$(TMEDA)	$\{(TMEDA)Li[(\mu_2\text{-}H)(\mu_2'\text{-}H)(\mu_3\text{-}H)BH]\}_2$	*b*	–	198
$LiBH_4$(TMTA)	$\{(TMTA)Li[(\mu_2\text{-}H)(\mu_2'\text{-}H)(\mu_3\text{-}H)BH]\}_2$	*b*	2367, 2343, 2271, 2225, 2154	148
$[H_2C(3,5\text{-}Me_2pz)_2]LiBH_4$	$\{[H_2C(3,5\text{-}Me_2pz)_2]Li[(\mu_2\text{-}H)(\mu_2'\text{-}H)(\mu_3\text{-}H)BH]\}_2$	*b*	2376, 2332, 2292, 2259, 2241, 2221, 2181, 2168, 2138	145
$(4,4'\text{-}Me_2bipy)LiBH_4$	$\{(4,4'\text{-}Me_2bipy)Li[(\mu_2\text{-}H)(\mu_2'\text{-}H)(\mu_3\text{-}H)BH]\}_2$	*b*	2390, 2293, 2227	145
$NaBH_4$(Diglyme)	$\{(Diglyme)Na[(\mu_2\text{-}H)(\mu_2'\text{-}H)(\mu_3\text{-}H)BH]\}_\infty$	*b*	–	199
$NaBH_4$(PMDETA)	$\{(PMDETA)Na[(\mu_2\text{-}H)(\mu_3\text{-}H)_2BH]\}_2$	*j*	2316, 2249, 2184	148
$NaBH_4$(TMTCN)	$\{(TMTCN)Na[(\mu_4\text{-}H)BH_3]\}_4$	*h*	2398, 2304, 2227	148
$Be(BH_4)_2$	$\{Be(\eta^2\text{-}BH_4)[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)_2B]\}_\infty$	*a*	2510, 2451, 2330, 2113, 2075, 1995	200, 201
$Sr(BH_4)_2(THF)_2$	$\{(THF)_2Sr[(\mu_2\text{-}H)(\mu_2'\text{-}H')(\mu_3\text{-}H)_2B]_2\}_\infty$	*i*	2372, 2313	157
$Ba(BH_4)_2(THF)_2$	$\{(THF)_2Ba[(\mu_2\text{-}H)(\mu_2'\text{-}H')(\mu_3\text{-}H)_2B]_2\}_\infty$	*i*	2353, 2308, 2241, 2216, 2186, 2169	157
Me_2AlBH_4	$\{Me_2Al[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)_2B]\}_\infty$	*a*	–	160
$Y(BH_4)_3$(DME)	$\{(DME)Y(\eta^3\text{-}BH_4)_2[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)_2B]\}_\infty$	*a*	2468, 2319, 2300, 2230, 2175	202
$(1,3\text{-}Bu^t_2C_5H_3)_2CeBH_4$	$\{(1,3\text{-}Bu^t_2C_5H_3)_2Ce[(\mu_2\text{-}H)(\mu_2'\text{-}H)(\mu_3\text{-}H)_2B]\}_2$	*i*	2290, 2180, 2100	203
$(1,3\text{-}Bu^t_2C_5H_3)_2SmBH_4$	$\{(1,3\text{-}Bu^t_2C_5H_3)_2Sm[(\mu_2\text{-}H)(\mu_2'\text{-}H)(\mu_3\text{-}H)_2B]\}_2$	*i*	2420, 2280	204
$(COT)(THF)_2NdBH_4$	$\{(COT)(THF)_2Nd[(\mu_2\text{-}H)(\mu_2'\text{-}H)(\mu_3\text{-}H)_2B]\}_2$	*i*	2255	205
ansa-$Cp'_2Yb(BH_4)_2Li(THF)_2$	$\{$*ansa*-$Cp'_2Yb[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)_2B][(\mu_2\text{-}H)_2(\mu_2''\text{-}H)_2B]Li(THF)_2\}_\infty$	*a*	–	206
$U(BH_4)_4$	$\{U(\eta^3\text{-}BH_4)_2[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)_2B]_2\}_\infty$	*a*	2552, 2538, 2262, 2182, 2087	207–210
$U(BH_4)_4(OMe_2)$	$\{(Me_2O)U(\eta^3\text{-}BH_4)_3[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)_2B]\}_\infty$	*a*	–	211
$U(BH_4)_4(OEt_2)$	$\{(Et_2O)U(\eta^3\text{-}BH_4)_3[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)_2B]\}_\infty$	*a*	–	211
$U(BH_4)_4(OPr_2)$	$\{(Pr_2O)_2U(\eta^3\text{-}BH_4)_3[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)_2B]U'(\eta^3\text{-}BH_4)_4\}$	*a*	–	212
$[Cr_2(Pr^iNCHNPr^i)_3]BH_4$	$[Cr_2(Pr^iNCHNPr^i)_3][(\mu_2\text{-}H)(\mu_2'\text{-}H)BH_2]$	*f*	2401, 2365, 2236, 2101	93
$Cr_3(BH_4)_6$(TMEDA)$_2Py_4$	$[(TMEDA)PyCr(\eta^2\text{-}BH_4)[(\mu_2\text{-}H)(\mu_2'\text{-}H)BH_2]_2[Py_2Cr'(\eta^2\text{-}BH_4)_2]$	*f*	–	93
$Mn_2(CO)_6(DPPM)(H)BH_4$	$[Mn(CO)_3]_2(\mu_2\text{-}DPPM)(\mu_2\text{-}H)[(\mu_2\text{-}H)(\mu_2'\text{-}H)BH_2]$	*f*	2472, 2333	173
$Mn_2(CO)_5(DPPM)(H)BH_4$	$[Mn(CO)_3](\mu_2\text{-}DPPM)(\mu\text{-}H)][(\mu_2\text{-}H)(\mu_2'\text{-}H)_2BH][Mn'(CO)_2]$	*e*	2487	174
$HFe_3(CO)_9(BH_4)$	$H[Fe(CO)_3]_3[(\mu_2\text{-}H)(\mu_2'\text{-}H)(\mu_2''\text{-}H)BH]$	*g*	2335	177
$[RuH(CO)(PPr^i_3)_2]_2(BH_4)(BF_4)$	$[RuH(CO)(PPr^i_3)_2]_2[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)_2B](BF_4)$	*a*	–	189
$[OsH(CO)(PPr^i_3)_2]_2(BH_4)(BF_4)$	$[OsH(CO)(PPr^i_3)_2]_2[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)_2B](BF_4)$	*a*	–	189
$[HC(CH_2PPh_2)_3RuH]_2(BH_4)(BPh_4)$	$[HC(CH_2PPh_2)_3RuH]_2[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)_2B]\}(BPh_4)$	*a*	–	213
$(C_6Me_6)_2Ru_2H_3(BH_4)$	$[(C_6Me_6)RuH_2](\mu_2\text{-}H)[(\mu_2\text{-}H)(\mu_2'\text{-}H)BH_2]$	*f*	2355, 2220	178
Co(DPPP)(BH_4)	$\{(DPPP)Co[(\mu_2\text{-}H)(\mu_2'\text{-}H)(\mu_3\text{-}H)BH]\}_2$	*b*	2415, 2030, 1985	214
$Cp^*_2Ir_2H_3(BH_4)$	$[(Cp^*IrH]_2(\mu_2\text{-}H)[(\mu_2\text{-}H)(\mu_2'\text{-}H)BH_2]$	*f*	2430, 2360, 2290, 2115, 2040	196
$\{[(Ph_3P)_2Cu]_2BH_4\}ClO_4$	$[(Ph_3P)_2Cu]_2[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)_2B]ClO_4$	*a*	2190, 2140, 2050	215, 216
$MeZnBH_4$	$\{MeZn[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)_2B]\}_\infty$	*a*	2255, 2215	217, 218
[cyclo-(*o*-$C_6F_4Hg)_3](BH_4)_2(Bu_4N)_2$	–	–	2300, 2035	219, 220
[cyclo-(*o*-$C_6F_4Hg)_3]_2(BH_4)(Bu_4N)$	–	–	2159, 2052	219, 220
$GaH_2(BH_4)$	$\{GaH_2[(\mu_2\text{-}H)_2(\mu_2'\text{-}H)BH](Ga'H_2)(\mu_2'\text{-}H)_2(\mu_2''\text{-}H)BH_2]\cdot(Ga''H_2)[(\mu_2''\text{-}H)(\mu''_2\text{-}H)_2BH]\}_\infty$	*e*, *f*	–	221

Note. The following designations are used: TMTA is trimethylhexahydrothiazine; bipy is bipyridine; TMTCN is 1,4,7-trimethyltriazacyclononane; *ansa*-Cp′ is methylenebis(3-trimethylsilylcyclopentadienyl), $CH_2(Me_3SiC_5H_3)_2$; DPPP is 1,5-bis(diphenylphosphino)pentane, $Ph_2P(CH_2)_5PPh_2$.

tetrahydroborate complexes are usually close to the sum of the Shannon ion radius of the metal[222] and the radius of the BH_4 ligand with the corresponding denticity [for η^3-BH_4, $r_i \simeq 1.36(6)$ Å and for η^2-BH_4, $r_i \simeq 1.6(1)$ Å].[223] In most cases, the results of this summation are in good agreement with experimental results. For example, for La(III) with a coordination number of 12 (r_i = 1.36 Å),[222] the lanthanum–boron distances calculated in this way (2.72 and 2.96 Å) are close to the values found experimentally (2.76 and 2.90 Å) in $[La(\eta^2\text{-}BH_4)_2(\eta^3\text{-}BH_4)_2(THF)_2]^-$ (see Ref. 18). However, when the coordination number is low and the complex contains bulky ligands, the calculated metal–boron distances deviate substantially from those found experimentally. In our opinion, these deviations point to a considerable influence of steric factors on the structural properties of the BH_4 ligands in the complexes. The use of so-

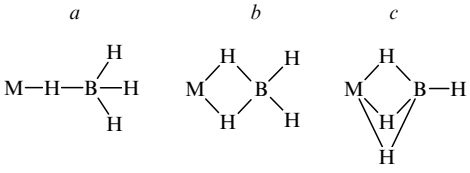


Figure 1. Coordination of terminal tetrahydroborate ligands in covalent complexes;
(*a*) monodentate η^1; (*b*) bidentate η^2; (*c*) tridentate η^3.

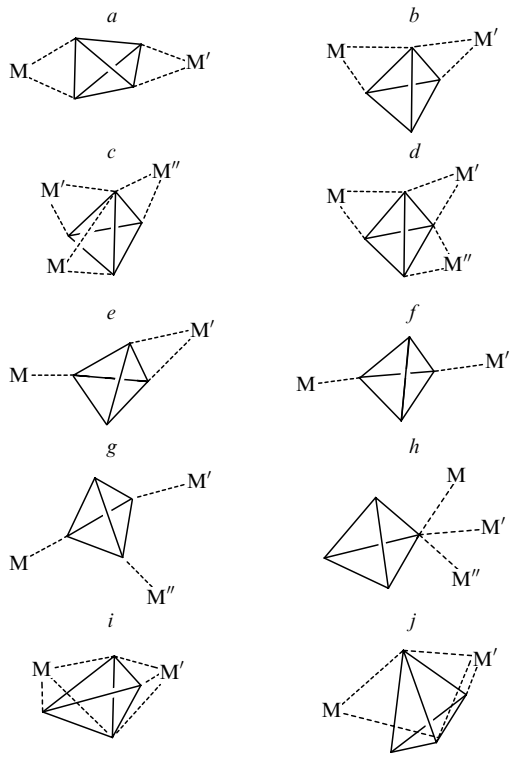


Figure 2. Coordination of bridging tetrahydroborate ligands in polynuclear complexes;
(*a*–*j*) see the text.

called effective coordination numbers, instead of the true values, has been proposed for compounds of this type.[223]

Valuable information concerning the type of the metal–ligand bond in the compounds under consideration can be gained using vibrational (IR and Raman) spectroscopy.[2,3] The observed absorption bands of BH_4 ligands with different denticities were assigned resorting to the studies of model compounds with known structures. Certain correlations between the spectral characteristics and structures of complexes were established. The most characteristic spectral region for the compounds in question is the region of stretching vibrations of the B–H bonds ($\sim$1650–2600 cm^{-1}). As a rule, a tridentate BH_4 group is responsible for an intense absorption band at $\sim$2450–2600 cm^{-1} [stretching vibrations of the terminal B–H bonds, ν(B–H$_t$)] and for an intense doublet of bands at about 2100–2200 cm^{-1} [stretching vibrations of the B–H bridging bonds, ν(B–H$_b$)]. A bidentate type of coordination shows itself as an intense doublet of bands in the region of 2400–2600 cm^{-1} and an intense band (perhaps, with a shoulder) at $\sim$1650–2150 cm^{-1}. Monodentate complexes are characterised by two broadened absorption bands, $\sim$2300–2450 and $\sim$2000 cm^{-1} (see Refs 2–5). Complexes in which the BH_4 group is bound to the metal ion *via* one or several M–H–B bonds have been named covalent tetrahydroborates.[2]

Unlike X-ray diffraction and IR spectroscopy data, the data of NMR spectroscopy for many tetrahydroborate complexes, both ionic and covalent, point to the equivalence of the four protons in the BH_4 ligand. The disagreement between the results obtained by different methods is due to the difference between the time scales of X-ray diffraction analysis and IR spectroscopy (characteristic time $\sim 10^{-18}$–10^{-20} s), on the one hand, and NMR (characteristic time $\sim 10^{-2}$–10^{-9} s), on the other hand, and to the fluxionality of these compounds on the NMR time scale, *i.e.*, the ability of the bridging and terminal protons of tetrahydroborate ligands to undergo fast intramolecular exchange.[2–5]

In terms of composition, tetrahydroborate complexes can be divided into two groups, homoleptic (containing one type of ligand) and heteroleptic (containing different ligands). Analysis of the vast experimental information accumulated to date permits one to establish the main types of tetrahydroborate complexes formed commonly by metals of each Group. Neutral homoleptic tetrahydroborates $M^n(BH_4)_n$ are typical of alkali and alkaline earth metals, beryllium, magnesium and aluminium. Among transition and post-transition metals, these complexes are known only for some lanthanides in the oxidation states +2 or +3, titanium subgroup metals, some actinides, zinc, cadmium and thallium(I).[1–5,224] Many neutral tetrahydroborates are able to attach additional BH_4 groups to give anionic complexes of the type $[M^n(BH_4)_{n+k}]^{k-}$ ($k = 1$–3); however, this anion stabilises noticeably only tetrahydroborates of 3*d* metals of the beginning of the transition metal row, from Sc to Fe. No homoleptic anionic complexes of cobalt, nickel, copper or Group I and V–VIII 4*d* or 5*d* transition metals have been obtained in a pure state.[225]

In most cases, in addition to BH_4 groups, tetrahydroborate complexes contain various stabilising ligands; the ligands found most often are ethers and polyethers, amines and polyamines (both cyclic and acyclic), cyclopentadienide anion derivatives and compounds of trivalent phosphorus (tertiary organic phosphines and phosphites). A large number of relatively stable complexes with ethers have been prepared for elements for which non-solvated neutral tetrahydroborates are known. A complex with tetrahydrofuran stable at room temperature is also formed by divalent manganese the ions of which possess a half-filled *d* shell.[99] For other transition metals, these complexes are either unstable [for example, the chromium complex $Cr(BH_4)_2(THF)_2$ decomposes at -20 °C] or unknown.[3]

Complexes with ligands such as halide, alkoxy or aryloxy anions and NO are rather rarely encountered in the chemistry of tetrahydroborates. Complexes with CO molecules as ligands are quite numerous but are mainly formed for Group VI–VIII metals. Anionic ligands (amides, alkoxides, aryloxides, *etc.*) stabilise effectively only tetrahydroborates formed by 3*d* metals of the beginning of the transition metal row. Examples of stabilisation of platinum metal complexes by cyclopentadienyl ligands are also documented. Unlike the above-mentioned ligands, amines and polyamines stabilise more efficiently complexes of metals from the middle to the end of each transition metal row.

Organic tertiary phosphines are the most efficient stabilising ligands for tetrahydroborates. In many cases, complexes contain hydride ligands together with phosphines. Tetrahydroborate complexes with these ligands are known for most transition metals but not for rare earth elements. The broad range of stabilising capacity of phosphines is stipulated by the broad range of variation of steric and electronic properties of these compounds. To fill the valence shells of metal atoms of the beginning of a transition metal row, a large number of electron-donating ligands are needed; in this case, strong electron donors having relatively small sizes such as trimethylphosphine and bis(dimethylphosphino)ethane are effective. On the contrary, to stabilise Group VIII metal complexes, a few ligands should shield the central atom having many valence electrons from contacts with the outer-sphere electron acceptors. In this case, the stability of complexes increases when they contain bulky ligands [P(cyclo-$C_6H_{11})_3$, PBu^t_3].

The most diverse types of tetrahydroborate complexes are formed by Group I, III and IV transition metals, although no complexes with CO ligands have been found for Group III metals and no complexes with CO or Cp ligands have been described for Group I transition metals. The tetrahydroborate complexes of nickel and palladium are least diverse (no complexes of this type are known for platinum), which is in sharp contrast with the extremely varied chemistry of coordination compounds of these metals with many other ligands (Ni, Pd, Pt are typical complex-forming elements). The typical stabilising ligands vary depending on the position of the metal in the Periodic Table. Whereas for

Table 4. The ability of ligands of different types to stabilise transition metal tetrahydroborates.

M	$M^n(BH_4)_n$	$[M^n(BH_4)_{n+1}]^-$	L in the complexes $M(BH_4)_nL_x$							Other ligands
			ethers	NR_2^-	Cp derivatives	CO	amines	H	PR_3	
REE	+	+	+	–	+	–	+ (Ln^{II})	–	–	+
Actinides	+	+	+	+	+	–	+ (U)	+	+	+
Ti, Zr, Hf	+	+	+	+	+	+ (Ti)	+	+	+	+
V, Nb, Ta	–	+ (V)	–	+ (V)	+	+ (Ta)	–	+	+	+
Cr, Mo, W	–	+ (Cr)	+ (Cr)	+ (Cr)	–	+	+ (Cr)	+	+	+
Mn, Re	–	+ (Mn)	+ (Mn)	–	–	+	+ (Mn)	+	+	+
Fe, Ru, Os	–	+ (Fe)	–	–	+ (Ru)	+	+	+	+	+
Co, Rh, Ir	–	–	–	–	+ (Ir)	+ (Rh, Ir)	+ (Co)	+	+	+
Ni, Pd	–	–	–	–	–	–	+ (Ni)	+	+	+
Cu, Ag	–	–	–	–	–	–	+ (Cu)	–	+	+
Pt, Au	–	–	–	–	–	–	–	–	–	–
Zn, Cd	+	+	+	–	–	–	+	+	–	+
Hg	–	–	–	–	–	–	–	–	–	+

Note. A plus sign means that for the given group of metals, tetrahydroborate complexes with ligands of this particular type are known, while a minus sign means that these complexes are unknown; the metal (or ion) to which the plus sign refers is given in parentheses.

complexes of Group III and IV transition metals, ethers and amines are commonly found ligands, in the case of Group I and V – VIII metal tetrahydroborates, compounds with these ligands are unusual. The ligands found most often for the latter type of metals are derivatives of tertiary organic phosphines, which are represented by only a few examples in the case of Group III and IV transition metal complexes.

The dependence of the types of stabilising ligands and complexes they form on the nature of the central transition metal atom can be followed by analysing the data of Table 4. It can be seen that the number of ligand types capable of efficient stabilisation of tetrahydroborate complexes decreases on passing from Group III and IV transition metals to Group VIII metals, especially to nickel and palladium for which only few examples of tetrahydroborate complexes are known. The decrease in the stability of tetrahydroborate complexes is even more pronounced on passing from 3*d* to 4*d* and 5*d* metals. As a result of these two trends, no tetrahydroborate complexes of 5*d* metals of the end of the transition row, *viz*., platinum or gold, have been characterised.

III. Transition metal complexes with terminal BH_4 ligands

The complexes of Group III and IV transition metals are most diverse regarding the mode of addition of the BH_4 ligands to the central atom (see Table 1). Compounds with any of the main types of coordination (see Fig. 1) can be found among complexes of these metals. Molecules containing BH_4 ligands coordinated to the same metal atom in two different modes are also known, for example, $Sc(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)_2(THF)_2$,[11] $Y(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)_2.(THF)_3$,[14] $(BP)Zr(\eta^3\text{-}BH_4)(\eta^2\text{-}BH_4)\cdot(THF)$.[64] The $Hf_2.(NPP)_2H_2(BH_4)_3$ complex contains simultaneously mono-, bi- and tridentate BH_4 groups.[83]

The structures of Group I and V – VIII metal complexes are much less studied (see Table 1); this can be explained by the sensitivity of many of them to oxygen and moisture and thermal instability and the difficulty of their synthesis and investigation arising thereupon. The structural chemistry of the tetrahydroborates of Group I and V – VIII transition metals is much scantier than that for Group III and IV metals. No complexes with tridentate BH_4 groups have been found for them; in the majority of their compounds, the BH_4 groups are bidentate ligands.

Among compounds of Group I and V – VIII transition metals, there are quite a few complexes with a monodentate coordination of tetrahydroborate ligands (~25% of the total number of structurally characterised complexes of the metals in question); this type of coordination is rather poorly studied. Nowadays, the existence of complexes with η^1-BH_4 groups has been reliably established by X-ray diffraction analysis and neutron diffraction. Structures of about 10 compounds of this type determined by X-ray diffraction analysis are documented; one of these compounds has also been studied by neutron diffraction. Taking into account the data of NMR spectroscopy, we would like to note that for Group I and IV – VIII transition metals, at least one example of an η^1-complex can be given for each group.

It is noteworthy that all η^1-complexes incorporate P-, N- or S-donor ligands (tertiary organic phosphines, amines and thia- and aza-macrocycles) possessing strong electron-donating properties. In most of these compounds, the central atom is linked to three or more phosphorus, nitrogen, or sulfur atoms.

In terms of the type of the stabilising ligand, the compounds considered can be divided into two groups, namely, complexes with P- and N-donor ligands, which differ markedly in physicochemical characteristics. The length of the $M-H_b$ bond in the former type of compound varies from 1.60 to 1.88 Å and the M – B distance ranges from 2.44 to 2.84 Å. The M – H – B bond is bent, the MHB angle ranging from 121 to 164°. The IR spectra of these compounds exhibit broad absorption bands in the ranges of 2300 – 2350 cm^{-1} [$\nu(BH_t)$] and ~2000 – 2100 cm^{-1} [$\nu(BH_b)$], which is consistent with the values predicted for η^1-complexes.[3] Resorting to the above-mentioned correlation between the structures and spectroscopic properties, the presence of monodentate BH_4 groups in L_3CuBH_4 type complexes [L = $PHPh_2$, $P(OPr^i)_2Ph$, PMe_2Ph] was demonstrated by IR spectroscopy. Study of the relationship between the structure of the copper compounds L_nCuBH_4 and the electronic and steric properties of phosphine ligands L showed that the complexes $L_3Cu(\eta^1\text{-}BH_4)$ with monodentate tetrahydroborate ligands are formed only when the electron-donating ligands L have a moderate size. A decrease in the electron-donating ability of the ligands, as well as an increase in their size, result in the complexes $L_2Cu(\eta^2\text{-}BH_4)$.[118]

However, compounds with N-donor ligands follow a different type of regularities. X-ray diffraction data point to an unusually long metal – boron distance (3.09 – 3.31 Å) in these compounds and IR spectra attest to the presence of BH_4^- anions.[130, 131] In solutions, these complexes appear to have ionic structure.[132]

For compounds with P-donor ligands, the difference between the experimentally determined metal – boron distance and the ion radius of the central atom is 2.0 ± 0.2 Å. In the complexes with N-donors, this difference is close to 2.4 Å, *i.e.* it substantially exceeds the radius of the BH_4^- anion (2.04 Å). This long metal – boron distance implies apparently the absence of covalent interaction between the central atom and the ligand, the monodentate

coordination of the BH_4 ligand in the crystals of these compounds being related to packing effects.

The NMR spectra of some monodentate complexes exhibit separate signals for the terminal and bridging protons, *i.e.* these compounds are less fluxional than complexes with tridentate BH_4 groups. It was shown in relation to iron compounds that an increase in the size of stabilising ligands increases the stereochemical rigidity of complexes, *i.e.* stabilises the η^1-coordination.[123] However, comparison of the structures of $Ti(\eta^2\text{-}BH_4)_2.(DMPE)_2$ (d^2-configuration of titanium) with $V(\eta^1\text{-}BH_4)_2.(DMPE)_2$ (d^3-configuration of vanadium)[53,54] and $CrH(\eta^2\text{-}BH_4)(DMPE)_2$ (d^4-configuration of chromium) with $FeH(\eta^1\text{-}BH_4)(DMPE)_2$ (d^6-configuration of iron),[94,123] which contain Ti(II) or V(II) and Cr(II) or Fe(II) ions with closely similar radii, demonstrates that η^1-coordination is not determined by steric factors alone. The η^1-coordination may also be facilitated by the d^3-configuration of V(II) and the d^6-configuration of Fe(II), which are favourable for the formation of octahedral complexes. The tetrahedral geometry, preferred for d^{10} ions for energy reasons, stipulates apparently the formation of the monodentate complexes $Cu(\eta^1\text{-}BH_4)(PMePh_2)_3$ and $Ag(\eta^1\text{-}BH_4).(PMePh_2)_3$, despite the fact that the ionic radius of Ag(I) is greater than that of Cu(I) and the volume of the silver coordination sphere is sufficient for η^2-coordination.[125,129] A η^1-coordination of BH_4 has been suggested previously for $RuH(\eta^2\text{-}BH_4).(PPh_3)_3$;[183] however, the fact that its IR spectrum differs from the IR spectra typical of η^1-complexes and resembles the spectrum of the complex $RuH(\eta^2\text{-}BH_4)(PMe_3)_3$, which has been characterised by X-ray diffraction analysis (see Table 1), points to a bidentate coordination of the BH_4 group in this complex.

Thus, in all the known cases, monodentate coordination of the BH_4 groups is due to the presence of stabilising ligands possessing definite properties (strong electron donors having a large size), *i.e.* this type of coordination is forced. Complexes with η^1-coordination of BH_4 groups might also be possible for ions with a different electron configuration provided that the coordination sphere contains a sufficient number of bulky electron-donating ligands. However, the currently available data do not allow one to predict unambiguously the appearance of η^1-coordination in each particular case.

The IR spectroscopic studies show that in most cases, experimental results are in good agreement with those predicted theoretically for the BH_4 groups of the corresponding coordination;[2–5] however, in some cases, the absorption bands due to the stretching vibrations of terminal B—H bonds occur at a substantially lower frequency than expected (see Tables 1, 2). Experimental data on the structures of tetrahydroborate complexes show that the idea of the three main types of coordination of the BH_4 ligands in so-called covalent tetrahydroborates is an idealisation. Among complexes of both Group III, IV and Group I, V–VIII transition metals, there are compounds with a distorted geometry of coordinated BH_4 ligands (unequal $M-H_b$ distances and MH_bB angles), which hampers unambiguous identification of the type of coordination. For example, in the structure of $Ti(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)_2(PMe_3)_2$, the tridentate coordination of the two BH_4 ligands is so distorted that these groups can be regarded as being coordinated through the B—H bonds (the Ti—B distance is 2.27 Å, Ti—H_b is 1.73 Å, the MH_bB angle is 112°).[52]

It has been noted that this coordination can be regarded as being characteristic of a hypothetical transition state in the activation of the methane molecule, isoelectronic with the tetrahydroborate anion. A similar distortion of a symmetrical coordination is also observed for some η^2-complexes, for example, for $(phen)(PPh_3)Cu(\eta^2\text{-}BH_4)$ (the Cu—B distance is 2.29 Å, Cu—H_b is 1.63 Å).[114] This type of coordination plays, apparently, an important role in the exchange of bridging hydrogen atoms and hydride ligands in the complexes $MH_3(BH_4)L_2$.[10] It has been noted above that the $M-H_b-B$ bridge in monodentate complexes is bent, and the MH_bB angle varies over wide limits (from 120 to 164°); hence, in some cases [for example, in $Hf_2(NPP)_2H_2(\eta^3,\eta^2,\eta^1\text{-}BH_4)_3$], the coordination of BH_4 groups found experimentally can be considered to be intermediate between mono- and bidentate coordinations.[83] The distortion of the geometry of coordinated ligands affects substantially the spectral properties of the complexes; therefore, in some cases, the denticity of the BH_4 groups cannot be identified unambiguously from the data of vibrational spectroscopy; for example, this is true for the copper and titanium compounds considered above.[52,114]

Compounds of Group III and IV transition metals possess clear-cut fluxionality; therefore, all the protons of the BH_4 ligands are equivalent on the NMR time scale.[2–5] Until recently, for none of the complexes of this type, were separate signals for the terminal and bridging protons of tetrahydroborate ligands distinguished in the NMR spectra, not even at low temperatures (for some compounds, studies were performed at ~150 K).[3] The activation energy for the exchange of terminal and bridging protons in these compounds equals ~5 kcal mol^{-1}, as estimated for $Cp_3U.(\eta^3\text{-}BH_4)$.[3] For compounds of Group IB metals, separate signals for bridging and terminal protons have not been identified either.[226] Only recently, was the first titanium compound reported {the complex $[Ti(CO)_4(\eta^3\text{-}BH_4)]^-[K(18C6)]^+$} for which the limit of slow proton exchange was attained at 178 K and individual signals for the terminal and bridging protons of η^3-BH_4 were observed.[65] The fact that the tetrahedral geometry of the BH_4^- anion in this complex is virtually non-distorted indicates a low contribution of the covalent constituent to the interaction of the central atom with this ligand. Note that in the analogous chromium and molybdenum complexes $[M(CO)_4(\eta^2\text{-}BH_4)]^-$, the tetrahydroborate ligand has a bidentate coordination. The unique structural and dynamic properties of the titanium complex (this is the only example of a tridentate tetrahydroborate group for which individual signals from the terminal and bridging protons were observed) are apparently due to the combination of the carbonyl groups (active π-acceptors and the most 'powerful' strong-field ligands) with an 'early' 3*d* metal in a low oxidation state in one molecule.

Many tetrahydroborates of Group V–VIII metals are much less fluxional than complexes formed by Group III and IV transition metals (see Table 2). At low temperature, individual signals of the terminal and bridging protons for both η^2- and η^1-BH_4 groups can be distinguished in the NMR spectra of these compounds. It is of interest that in some cases, bridging protons of the η^2-BH_4 groups account for two separate signals and the exchange of these non-equivalent bridging protons with terminal protons occurs at different rates.[171] In some complexes, this proton exchange does not proceed at a noticeable rate even at room temperature, or at higher temperatures. Thus for one of the least fluxional tetrahydroborates $Os(\eta^2\text{-}BH_4)H_3(PPr^i_3)_2$, this process cannot be observed even at 360 K. The activation energy for the exchange of the terminal and bridging protons in this compound cannot be determined experimentally because this compound decomposes at higher temperatures. According to estimates,[10] this energy is greater than 20 kcal mol^{-1}. At 300 K, the bridging protons in this compound undergo fast exchange with the hydride ligands $(Os)H_3$ (activation energy ~13 kcal mol^{-1}). The results of experimental studies and quantum-chemical calculations for $Os(\eta^2\text{-}BH_4)H_3(PPr^i_3)_2$ provide grounds for suggesting that the exchange of bridging hydrogen atoms $(B)H_b$ with the hydride ligands $(Os)H_t$ without participation of the terminal hydrogen atoms $(B)H_t$ proceeds *via* a transition state in which the metal is coordinated to the B—H bond.[10]

The data presented above demonstrate that the existing view about the exceptionally high fluxionality of transition metal tetrahydroborate complexes needs to be corrected. Individual signals for the terminal and bridging protons cannot be observed (with only one exception[65]) only for compounds of Group I, III and IV transition metals. Among Group V–VIII transition metal compounds, many complexes do give rise to separate NMR signals for the terminal and bridging protons of the BH_4 ligands. The fluxionality decreases with an increase in the size of the

stabilising ligands. This has been shown in relation to the iron complex $FeH(BH_4)L_2$ (L = DMPE, DEPE, DPrPE) and a niobium complex with the Cp and Cp* ligands, respectively.[123, 169] The results of analysis of the activation energy for the exchange of bridging and terminal protons suggest that the fluxionality of the complexes decreases also on passing from Group V metals to Group VIII metals and from 3*d* metals to 4*d* or 5*d* metals (see Table 2). Thus, the decrease in the fluxionality of tetrahydroborates occurs in the same direction as the decrease in their thermal stability mentioned above. The correlation observed between these properties might be due to the fact that a decrease in the fluxionality is indicative of an increase in the degree of covalency of the $M-H_b$ bond, which increases the probability of decomposition of tetrahydroborate complexes by the oxidative addition mechanism ($MBH_4 \rightarrow HMBH_3$).

IV. Possible reasons for the differences in the structural and dynamic properties of tetrahydroborate complexes

What is the reason for the so sharp differences in the types of ligand coordination and in the structural and dynamic properties of the complexes formed by Group III and IV transition metals and those formed by Group I, V–VIII transition metals? The attempts to rationalise the structure of tetrahydroborate complexes in terms of the Coulomb interaction between the BH_4^- anions and metal cations (with the assumption that enhancement of the Coulomb forces should increase the degree of covalence of the metal–boron bond and the denticity of the BH_4 ligand [227]) do not provide satisfactory results. The attractive force between the anion and the central atom in many complexes of Group I, V–VIII transition metals should be greater than that in Group III and IV metal complexes because the ratio of the ion charge to the ionic radius squared (z/r^2) for, for example, Fe(II), Co(II) and Ni(II) is greater than this ratio for U(III) or cerium subgroup lanthanides. Nevertheless, the denticity of the BH_4 ligand is lower in the former type of complexes.

Since the oxidation number of the central atoms in most of the Group I, V–VIII transition metal tetrahydroborates is +2, while that in the complexes of Group III and IV transition metals is +3 or +4, one can suggest that the difference in the ligand denticity is related to the oxidation state of the central atom. However, this suggestion is at variance with the existence of a number of bidentate complexes of Group V–VIII transition metals containing the central atom in the +3 and +4 oxidation state [for example, $Ir(\eta^2\text{-}BH_4)H_2(PBu^t_3)_2$, $WH_3(\eta^2\text{-}BH_4)(PMe_3)_3$, $OsH_3(\eta^2\text{-}BH_4)(PPr^i_3)_2$]; conversely, complexes of divalent ytterbium contain tetrahydroborate groups coordinated in the tridentate manner (see Table 1).

The most widespread hypothesis states that the tetrahydroborate ligand in the complexes is linked to the central atom *via* covalent two-electron three-centre M–H–B bonds and is isolobal to the chloride, allyl or cyclopentadienyl anion, *i.e.* it acts as a two-, four- or six-electron donor, depending on the denticity. According to this hypothesis, the type of coordination (η^n) of the BH_4 ligand corresponds to the number *n* of electron pairs provided by this ligand and the ligand denticity is determined by the tendency of the central atom to fill the outer electron shell and can be predicted using the effective atomic number (EAN) rule.[228–230]

However, the attempts to apply this approach to a broad range of objects showed that predictions based on this hypothesis often do not comply with experimental data regarding both chemical and physical properties of tetrahydroborate complexes, or with the EAN rule. For example, in conformity with this hypothesis, $Cu(\eta^2\text{-}BH_4)(phen)(PPh_3)$ and $Cp_2M(\eta^2\text{-}BH_4)_2$ (M = Zr, Hf) should be 20-electron complexes, $Y(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)_2(THF)_3$ should be 22-electron, $M(\eta^3\text{-}BH_4)_4$ (M = Zr, Hf) should be 24-electron, and $[Zn(\eta^2\text{-}BH_4)_4]^{2-}$ should even be a 26-electron complex.[231] This hypothesis cannot also interpret the change in the type of coordination in the pairs of isoelectronic complexes $Sc(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)_2(THF)_2$, $Y(\eta^3\text{-}BH_4)_3(THF)_2$ and $(MeOCH_2CH_2C_5H_4)_2Pr(\eta^3\text{-}BH_4)$, $(MeOCH_2CH_2C_5H_4)_2Yb(\eta^2\text{-}BH_4)$. The paramagnetism of the vanadium $V(\eta^2\text{-}BH_4)_3(PMe_3)_2$ (μ_{ef} = 2.5 μ_B),[84] chromium $(TMEDA)Cr(\eta^2\text{-}BH_4)_2$ (μ_{ef} = 4.8 μ_B),[93] and cobalt $Co(\eta^2\text{-}BH_4)[MeC(CH_2PPh_2)_3]$ (μ_{ef} = 3.1 μ_B) [109] complexes considered in terms of this hypothesis does not agree with the denticity of the BH_4 ligands found for these complexes. The Lewis acidity of the allegedly 18-electron complex $Zn(\eta^2\text{-}BH_4)_2$ (see Ref. 231) and the 24-electron complexes $M(\eta^3\text{-}BH_4)_4$ (M = Zr, Hf) cannot be explained either.[232, 233] When the number of electrons is calculated in this way, deviations from the EAN rule are observed for many structurally characterised transition metal tetrahydroborates; the deviation increases with an increase in the number and denticity of the BH_4 ligands in the complex, which indicates that this method overestimates the number of electrons donated by the tetrahydroborate ligand.

It should also be noted that, in accordance with the views considered above,[222–230] the strength of the metal–tetrahydroborate ligand bond should increase with an increase in the number of M–H 'covalent' bonds, *i.e.* with an increase in the ligand denticity. This, in turn, should result in an increase in the stereochemical rigidity of complexes on passing from monodentate to bi- and then to tri-dentate coordination of BH_4 groups. However, experimental results point to an opposite trend, namely, complexes with η^2- and even η^1-BH_4 groups are stereochemically more rigid than complexes with η^3-BH_4 ligands.

Thus, the hypothesis that, depending on its denticity, the BH_4 group is isolobal to chloro, allyl or cyclopentadienyl ligand cannot explain and predict correctly the chemical, physical or structural properties of transition metal tetrahydroborates. Data on a decrease in the fluxionality of complexes with η^3-BH_4 groups with respect to the complexes with η^2-BH_4 and η^1-BH_4 groups point to a low contribution of covalent interaction to the bond of the metal with the BH_4^- anions, at least, for Group III and IV transition metals. This conclusion is in agreement with the results of calculations carried out for the $L_{4-n}Cu-H_n-BH_{4-n}$ complexes (*n* = 1, 2, 3), which showed a largely ionic character of the $Cu-H_n-BH_{4-n}$ bond and electrostatic nature of the interaction between the coordinated copper atom and the BH_4^- anion with a relatively small contribution of the covalent bond.[234] This conclusion is also consistent with the results of a study of copper tetrahydroborate complexes by mass spectrometry with extraction of ions from the solution (electro-spray mass spectrometry).[235, 236]

The change in the type of coordination of the BH_4 ligands in Group III and IV transition metal complexes is much better explained by the influence of purely steric properties of ligands if one assumes that these complexes tend to fill the coordination sphere of the central atom as fully as possible and that a tridentate coordination of the BH_4 group to the metal atom, which implies the largest volume occupied by this group, is the most favourable. It is assumed that this type of coordination is always realised whenever it is allowed by the spatial conditions in the complex and that transition to other types of coordination is induced by the influence of steric factors. On this basis, a procedure for the calculation of the degree of occupancy of the metal coordination space was developed and convincing examples confirming the efficiency and predictive capacity of this approach were cited.[237] † The trend to fill the coordination sphere of the central atom as fully as possible and the high coordination numbers typical of tetrahydroborates of Group III and IV transition metals attest to a high degree of ionicity of the $M-BH_4$ bond, which is consistent with the substantial fluxionality of these compounds.

Nevertheless, several examples demonstrate that the scope of this approach is also limited. It is mainly applicable to Group III

† Unfortunately, only few steric constants of ligands are given in the study cited,[237] which narrows down the scope of application of this method.

and IV transition metal compounds, although with exceptions. For example, only half of the BH_4 groups in the $[La(\eta^3\text{-}BH_4)_2.(\eta^2\text{-}BH_4)_2(THF)_2]^-$ anion are coordinated as η^3-ligands, despite the fact that the metal coordination sphere is filled only to 86%.[18] This approach cannot be used to interpret the structure of complexes formed by transition metals of other groups. For example, in the $[Mn(\eta^2\text{-}BH_4)_3(THF)]^-$ and $[Zn(\eta^2\text{-}BH_4)_3]^-$ anions, the BH_4 ligands have η^2-coordination,[100, 101, 134] although the coordination spheres of the central atom are filled only to 86% and 75%, respectively.

Thus, in the general case, the difference between the types of coordination of the BH_4 ligands in transition metal compounds cannot be explained by either the influence of the oxidation state of the central atom, or the different electrostatic interaction of the metal with the ligands, or by the 'tendency' of the central atom to fill the outer electron shell, or by the influence of spatial factors.

Analysis of the data presented in Tables 1, 2 suggests that the main factor determining the differences between the structures and dynamics of the tetrahydroborate complexes of Group III and IV transition metals, on the one hand, and Group I, V – VIII metals, on the other hand, is the difference between the electronic configurations of the central atoms.

The electronic configuration of Group III and IV transition metals in compounds with tridentate tetrahydroborate ligands (except for the complex of zerovalent titanium with carbonyl groups[65]) is d^0 (or d^1 in the case of complexes of trivalent titanium). In the complexes of Group I, V – VIII transition metals, the central atom with the d^n-configuration ($n = 2-10$) has at least two electrons not involved in the formation of the chemical bonds in the outer d shell. The fact that no examples of structurally characterised complexes of these metals with tridentate BH_4 ligands are available suggests that the presence of two or more electrons in the outer d shell destabilises the η^3-coordination and, therefore, the η^2-coordination becomes more favourable from the energy standpoint. Thus, whereas the bidentate coordination is sterically forced in complexes with central atoms having the d^0- and d^1-configuration, in the case of ions with d^n-configurations ($n = 2-10$), it is the η^2-coordination that is realised without steric restrictions.

The increase in the stereochemical rigidity of complexes on passing to compounds of Group V – VIII metals can be accounted for by the presence of electrons in the outer d shell which do not participate in the formation of chemical bonds and decrease the energetic profitability of the most probable rearrangement pathway $\eta^2-\eta^3-\eta^{2\prime}$.[57] Indeed, quantum-chemical calculations[10] showed that $\eta^2-\eta^1-\eta^{2\prime}$ is an energetically more favourable pathway for the exchange of the bridging and terminal protons of the BH_4 group in the complex $Os(\eta^2\text{-}BH_4)H_3(PPr^i_3)_2$.

In conformity with the above-noted crucial influence of the electronic configuration of the central atom on the structural and dynamic properties of the tetrahydroborate ligands in the complex, derivatives of titanium group metals with the oxidation number +2 should contain bidentate BH_4 ligands. In fact, no examples of Ti(II) compounds with tridentate BH_4 groups are available; in the d^2-complexes, $Cp^*Ti(\eta^2\text{-}BH_4)[(Me_2PCH_2)_3.SiBu^t]$ and $Ti(\eta^2\text{-}BH_4)_2(DMPE)_2$, the BH_4 groups are coordinated as bidentate ligands.[54, 55] However, in the d^0-complex $Yb(\eta^3\text{-}BH_4)_2(Py)_4$, these ligands are tridentate,[22] despite the substantially greater ionic radius of the central atom, which decreases the Coulomb interaction.

In this connection, we would like to mention the well-known influence of lone electron pairs on the structure of coordination compounds explained by repulsion of the coordinated ligands from non-bonding electrons.[238] It was noted that, when the number of non-bonding d electrons is 1 to 3, their effect on the structural properties of molecules is normally too low to be detected experimentally. However, the examples considered above demonstrate that the type of coordination and the dynamic behaviour of the BH_4 ligand change crucially even in the presence of two non-bonding outer d electrons.

As any other corollary based on the generalisation of experimental data, this assumption leaves room for exceptions the discovery and analysis of which would result in further development of the views on the structures of the compounds considered. To verify the assumption concerning the reasons for the differences in the modes of coordination and dynamic properties of BH_4 ligands, it is necessary, in particular, to study complexes of Group IV transition metals with the central atom in a low oxidation state and to develop methods for the synthesis and study of compounds of Group V – VIII metals in high oxidation states.

V. Complexes of post-transition metals with terminal BH_4 ligands

The assumption that metal d electrons destabilise the η^3-coordination of the BH_4 groups more significantly than the η^2-coordination relied on analysis of the results of quantum-chemical calculations for complexes with central d^{10} ions.[239, 240] It was suggested that this destabilisation should decrease the difference between the energies of η^2- and η^3-coordinated groups and thus enhance the fluxionality of tetrahydroborate complexes. Indeed, no data about non-equivalence of the terminal and bridging protons in the tetrahydroborate complexes with d^{10}-configuration of the central atom can be found in the literature. Moreover, experimental data point to specific properties of the complexes in which the outer d shell of the metal ions is either half or completely filled (d^5 or d^{10}). Thus Mn(II), Cu(I) and Zn(II) complexes are much more numerous and thermally stable than complexes of other Group V – VIII transition metals or post-transition metals.

It could be suggested that the presence of a filled d shell influences not only the thermal stability of the complex but also the mode of coordination of the BH_4 groups. However, it can be seen that both post-transition metals (Zn, Cd, Hg, Ga, In) having a closed outer d^{10} shell and Group I and V – VIII transition metals having d^n-configurations ($n = 2-10$) tend to be coordinated by BH_4 in a bidentate fashion even in those cases where steric factors are favourable for η^3-coordination (see Table 1). Indeed, the complexes $Zn(\eta^2\text{-}BH_4)_2$ and $[Zn(\eta^2\text{-}BH_4)_3]^-$ contain bidentate BH_4 ligands, despite the fact that the metal coordination sphere is not 100% full {in $[Zn(\eta^2\text{-}BH_4)_3]^-$, it is only 75% full}. Apparently, even a closed outer d-shell destabilises η^3-coordination, although, due to its higher symmetry, a less pronounced destabilisation of the complex should be expected in this case.

The paucity of post-transition metal complexes the structures of which are known can be explained by their low thermal stability (see Table 1). The complex $Cp(CO)_2FeGa(\eta^2\text{-}BH_4)[(CH_2)_3NMe_2]$ is the only example, among gallium tetrahydroborate complexes with terminal BH_4 groups, the structure of which has been established by X-ray diffraction analysis.[143] The structural data for other gallium complexes presented in Table 1 have been obtained by gas phase electron diffraction analysis. No examples of structurally characterised tetrahydroborate complexes of mercury, indium or thallium can be found in the literature. However, the conclusion about bidentate coordination of the BH_4 ligand in $Me_2In(\eta^2\text{-}BH_4)$ has been drawn on the basis of IR-spectroscopic data.[144] The IR spectra of the tetrahydroborate complexes of post-transition metals reported in the literature generally comply, in the region of stretching B – H vibrations, with those expected for bidentate BH_4 groups (see Table 1).

The synthesis of tetravalent germanium and tin tetrahydroborates $M(\eta^3\text{-}BH_4)_4$ (M = Ge, Sn) has been reported;[241] they were obtained as solid compounds stable in air up to 473 K and containing tridentate (according to IR spectroscopy) tetrahydroborate ligands. An estimate of the degree of filling of the coordination sphere in these compounds, which we performed using published data,[223, 237] showed that in the case of Ge(IV), η^3-coordination of the four BH_4 groups is unlikely because the coordination sphere of the central atom is overcrowded, while the Sn(IV) coordination sphere in $Sn(\eta^3\text{-}BH_4)_4$ should be filled to 100%. Covalent tetrahydroborates with filled coordination

spheres of the metal atoms should be volatile compounds unstable in air, like $Zr(\eta^3\text{-}BH_4)_4$. Therefore, the properties described for tetravalent germanium and tin tetrahydroborates, and even the mere fact of existence of these compounds, appear doubtful. It is noteworthy that reports concerning the syntheses of unusual tetrahydroborate complexes of transition metals, such as Cp_3CeBH_4 [242] and $Cp_2MO(\eta^2\text{-}BH_4)_2$ (M = Mo, W),[243] have been published and repeatedly cited, although subsequent attempts to reproduce them failed.[244, 245]

VI. Complexes of Group IA and IIA metals and aluminium with terminal BH_4 ligands

The structures of alkali and alkaline earth tetrahydroborate complexes are little studied. Among alkali metal complexes, lithium compounds have been studied most comprehensively. Table 1 presents several examples of complexes of univalent lithium with η^2- and η^3-coordinated BH_4 ligands. Antsyshkina *et al.*[146] believe that the complex $LiBH_4$(18C6) in the crystalline state contains a η^1-coordinated BH_4 group. The same structure was proposed [146] for $NaBH_4$(15C5).[150] However, the conclusions about the monodentate coordination of the tetrahydroborate ligands are inconsistent with the experimental data on the M···B distances in these complexes, which are close to the value expected for η^2-BH_4.[223] Despite the fact that no data on the structures of tetrahydroborates of heavier metals (K, Rb, Cs) are available to date, it can be suggested that these metals, like lithium, form compounds with all the main types of coordination of BH_4. The difference between the structures of $Li(\eta^3\text{-}BH_4)[HC(3,5\text{-}Me_2pz)_3]$ and $Cd(\eta^2\text{-}BH_4)[HB(3,5\text{-}Me_2pz)_3]$, noted by Reger *et al.*,[145] namely, the fact that the BH_4 group is coordinated in the bidentate fashion to the Cd(II) ion having a greater size and a higher charge, whereas it is coordinated as a tridentate ligand to the Li(I) ion, can be understood in view of the assumption about destabilising influence of outer *d* electrons.

The similarity of the structural and spectral properties of $TlBH_4$ to those of alkali metal tetrahydroborates [1, 2] is also consistent with this assumption because the closed $5d^{10}$ shell of the Tl(I) ion is shielded by the filled $6s^2$ shell, which diminishes the destabilising influence.

The type of BH_4 coordination in $CpBe(\eta^2\text{-}BH_4)$ could not be established unambiguously from electron diffraction data. The conclusion about the bidentate coordination of this ligand to the beryllium atom was drawn resorting to the data of IR spectroscopy.[151, 152] The denticity of BH_4 ligands in alkaline earth metal complexes (Ca, Sr, Ba) corresponds to that expected on the basis of steric considerations — BH_4 groups accomplish tridentate coordination whenever the spatial possibility exists. No structural data pointing to the possibility of η^3-coordination of BH_4 groups in magnesium or aluminium complexes are currently available. In this connection, recall that the ionic radii of Al(III) and, especially, Be(II) are much smaller than those of transition metals.[222]

The type of coordination of tetrahydroborate ligands in the metal complexes in question cannot be determined from the data of NMR spectroscopy; these data attest to equivalence of all the four protons in the BH_4 ligand.[145, 147, 148, 157, 161] The data of IR spectroscopy for alkali and alkaline earth metal complexes do not conform to any particular type of coordination of the tetrahydroborate groups either.[145, 147, 148, 157]

The structures of the tetrahydroborate complexes with the central d^0-metal ions in the oxidation state +1 as well as complexes with the d^n-metal central ions ($n = 2-10$) cannot be explained in terms of the principle of the maximum occupancy of the coordination sphere. Calculations using this principle [237] provide the best results in the case of complexes with $d^0(d^1)$-metal central ions in the oxidation states +3 or +4 and with ionic radii ranging from 0.7 to ~1 Å. Calculations performed in conformity with the data reported by Edelstein [223] show that tridentate coordination of BH_4 groups in tetrahydroborates of metals with ionic radii of less than 0.68 Å (the difference between the radii of the ionic and tridentate forms of BH_4) requires that the metal–boron distances be smaller than the radius of the BH_4^- anion. Therefore, the deviations from the principle of the maximum occupancy of the coordination sphere observed for these ions can be attributed to the mutual repulsion of ligands. For d^0-metal ions in the oxidation state +2, this principle can be used to estimate the probable denticity of the BH_4 ligands; however, the maximum occupancy of the metal coordination sphere is seldom encountered. Apparently, under normal conditions, the number of neutral ligands (for example, ethers) these ions can hold is insufficient to fill completely their coordination sphere. Thus, the scope of application of the principle of the maximum occupancy of the coordination sphere of the central atom for predicting the structures of tetrahydroborate complexes is mainly limited to complexes with central d^0-metal ions in the oxidation states +3 and +4.

VII. Tetrahydroborate complexes with bridging BH_4 ligands

The structurally characterised compounds with bridging tetrahydroborate groups are presented in Table 3. Comparison of the data of Tables 1 and 3 shows that alkali metal complexes with bridging BH_4 ligands are as prevalent as complexes with terminal tetrahydroborate ligands. On passing to alkali earth metals, lanthanides and actinides, the proportion of compounds with bridging BH_4 groups in the whole set of structurally characterised compounds gradually decreases; no structurally characterised bi- or polynuclear complexes of Group IV and V transition metals with tetrahydroborate bridges between the metal atoms are known. The trend to form complexes with bridging BH_4 groups then starts increasing again and, for Group VIII metals, the fractions of complexes with known structures containing terminal and bridging BH_4 groups are nearly equal. These data suggest that the formation of bridged compounds is facilitated by a decrease in the charge and an increase in the radius of the complex-forming ion.

The most frequently encountered polynuclear complexes (14 of 39, see Table 3) are those in which two metal atoms are bound in the η^2-fashion to the opposite edges of a BH_4 tetrahedron (see Fig. 2 *a*). None of the tetrahedron vertices belong simultaneously to both metal atoms. Each hydrogen forms μ_2-bridges between boron and the metal, *i.e.* the BH_4 groups are generally tetradentate. Depending on the oxidation state of the metal, the number of BH_4 tetrahedra, the nature of the stabilising ligands and crystallisation conditions, this type of coordination of bridging groups results in the formation of dimers,[189, 212, 213, 216] infinite polymer chains,[160, 200, 202, 217] a two-dimensional network,[210] or a three-dimensional network.[147, 207, 208] Apparently, three-dimensional structures of this type are also formed in some non-solvated compounds $M^n(BH_4)_n$ ('ionic' tetrahydroborates).

In a less abundant (six complexes) type of coordination, the BH_4 group is bound by two edges to two metal atoms and the edges participating in the coordination share a vertex (μ_3-H). One hydrogen remains free from binding to the metal atoms; thus, the BH_4 groups are in total tridentate (see Fig. 2 *b*). This pattern of coordination results most often in the formation of dimeric complexes [145, 148, 198, 214] and in some cases, polymer chains.[199]

There is only one compound ($LiBH_4 \cdot Et_2O$) in which the BH_4 group is coordinated to three metal atoms (to each of them, by an edge); these three edges share a vertex (μ_4-H, see Fig. 2 *c*).[147, 197] In the crystals of $LiBH_4$(MeOBu^t), the BH_4 group is also coordinated by its edges to three metal atoms; however, there is no vertex common to these three edges (see Fig. 2 *d*). In these cases (see Fig. 2 *c*,*d*), all the four hydrogen atoms are involved in the formation of bridging bonds, *i.e.* the BH_4 group is tetradentate.

The η^1,η^2-bridging coordination is represented by two examples, $Mn_2(CO)_5(DPPM)H(BH_4)$ and $GaH_2(BH_4)$; in this case, one metal atom is coordinated to an edge of the tetrahedron, while the other one is bound to the opposing vertex (see Fig. 2 *e*).[174, 221] The

η^1,η^1-coordination according to which each of the two metal atoms is bound to one tetrahedron vertex (see Fig. 2*f*) is represented by six examples.[93, 173, 178, 196, 221] This gives rise to a chain or a ring with the M—H—BH_2—H—M sequence of bonds; two hydrogen atoms remain in the terminal positions.

The complex $GaH_2(BH_4)$ in the crystalline state forms a polymer chain consisting of alternating BH_4 tetrahedra with the types of coordination shown in Fig. 2*e*,*f*, so that the coordination numbers of the gallium ions are 4 and 6.[221]

There exists one example, $HFe_3(CO)_9(BH_4)$, of η^1,η^1,η^1-coordination of the BH_4 ligand where three metal atoms of the cluster are bound to three vertices of the BH_4 tetrahedron (three μ_2-H bonds; the overall denticity of the tetrahydroborate ligand is η^3, see Fig. 2*g*).[177] Conversely, in the Na_4B_4 heterocubane core of the $[NaBH_4(TMTCN)]_4$ tetramer, each three neighbouring sodium atoms are linked to the same vertex of the BH_4 tetrahedron (μ_4-H bond; the total denticity of the BH_4 group is η^1, Fig. 2*h*).[148]

Among mercury complexes, two compounds, [cyclo-(*o*-$C_6F_4Hg)_3]\cdot(BH_4)_2(Bu_4N)_2$ and [cyclo-(*o*-$C_6F_4Hg)_3]_2(BH_4)$. .(Bu_4N), have been isolated in an individual state.[219] Their structures have not been determined. Relying on the results of quantum-chemical calculations, it was assumed that the BH_4 ligand in [cyclo(*o*-$C_6F_4Hg)_3]_2\cdot(BH_4)(Bu_4N)$ is linked to one mercury macrocycle as shown in Fig. 2*g* and to one more macrocycle as shown in Fig. 2*h*,[220] *i.e.* this group is supposed to be connected simultaneously to six metal atoms.

A type of coordination in polynuclear complexes represented rather widely (six structures) is the coordination according to which one or two metal atoms are bound to a face of the BH_4 tetrahedron, which corresponds to η^3-coordination in mononuclear complexes (see Fig. 2*i*, total denticity η^4, and Fig. 2*j*, total denticity η^3). However, as in the case of mononuclear complexes, this coordination pattern is encountered only for metal ions having no outer *d* electrons, *i.e.* sodium,[148] strontium(II), barium(-II),[157] cerium(III),[203] samarium(III)[204] and neodymium(III),[205] whereas no examples of face coordination (η^3) are known for d^n ions ($n = 2-10$) (see Table 3).

In the NMR spectra of complexes of Group I, II, III and IV metals with BH_4 bridges, separate signals for the terminal and bridging protons have not been detected. The non-equivalence of protons of the bridging BH_4^- ligands has been observed in the NMR spectra of complexes of Group VII–VIII transition metals.[173, 174, 177, 178, 188, 196] Thus, the structure and the dynamic behaviour of polynuclear compounds with BH_4 bridging groups also does not contradict the assumptions made in this study.

The data presented in Table 3 demonstrate a fundamental difference between the complexes with central d^0-metal ions and the complexes with d^n transition metal ions ($n = 2-10$), namely, in the case of alkali and alkaline earth metals, lanthanides and uranium, the tetrahydroborate bridges connect neutral mononuclear molecular units, which results in a fuller occupancy of the metal coordination sphere and corresponds to the non-directionality and non-saturability of the mainly ionic M—BH_4 bond in these compounds. In the case of Group I and V–VIII transition metals, the tetrahydroborate bridges are formed between cationic species or, in most cases, between metal atoms bound into a cluster and located close to each other. The example of the cobalt complex $[Co(DPPP)(BH_4)]_2$ seemingly contradicts this conclusion. However, the low magnetic moment of this complex points to the presence of a metal—metal bond.[214] Hence, in this case, too, the formation of the tetrahydroborate bridges is favoured by the presence of a bond between transition metal atoms. Among post-transition metal complexes, there are compounds with polymer chains consisting of neutral molecules connected *via* tetrahydroborate bridges, for example, $[MeZnBH_4]_\infty$[217, 218] and $[GaH_2(BH_4)]_\infty$.[221]

The fluxionality, η^3-coordination and the trend for the maximum occupancy of the coordination sphere are as typical of lanthanide and actinide complexes as of complexes formed by *d* metals with d^0 central ions. Therefore, it can be concluded that *f* electrons do not influence the properties of tetrahydroborate complexes as substantially as outer *d* electrons. It has been suggested[5, 207] that *f* orbitals participate in the formation of the bonds of the central atom with the BH_4 groups. However, in our opinion, the available data do not provide grounds for this suggestion.

In the structures which have now been determined, one to three metal ions are connected to one BH_4 group *via* its vertices or edges, or one or two metal ions are coordinated to this BH_4 group *via* faces. The metal ions in one structure can be coordinated both in the same way and in different ways; however, not all the possible combinations of various types of coordination have been confirmed experimentally. Thus a complex in which three metal ions are bound to the same vertex of the BH_4 tetrahedron in the monodentate fashion is known but there are no examples of complexes in which two or more metal ions are coordinated in the bidentate fashion to the same edge or in the tridentate fashion to the same face of the tetrahedron. Examples of structurally characterised complexes in which four or more metal ions are linked to one BH_4 group or examples of heteronuclear complexes in which this group serves as a bridge between ions of different metals cannot be given either. In the majority of polynuclear complexes ($\sim 60\%$ of the total number), all the four hydrogen atoms of the BH_4 groups are involved in coordination, *i.e.* they are formally tetradentate ligands (see Fig. 2*a*,*c*,*d*,*j*). About one-fourth of the complexes studied (see Fig. 2*b*,*e*,*g*) contain BH_4 ligands with one non-coordinated hydrogen atom. There are only a few polynuclear complexes with tetrahydroborate bridges formed by one (see Fig. 2*h*) or two (see Fig. 2*f*) hydrogen atoms.

Unlike compounds with terminal tetrahydroborate ligands, for bridging complexes, no correlation has been found between the data of IR spectroscopy and the types of coordination of bridging groups.

It has been noted[198] that the hypothesis of three-centre two-electron type of the M—H—B bond is inapplicable for calculation of the EAN in the compounds with bridging BH_4 groups.

VIII. Conclusion

Analysis of experimental data on the structure of tetrahydroborate complexes makes it possible to elucidate a series of correlations between the structural or dynamic properties of these compounds and the nature of the central atom and stabilising ligands.

Compounds of Group III and IV transition metals (lanthanides, U, Ti, Zr, Hf) have been studied most comprehensively. In addition to the diversity of stabilising ligands, these complexes are characterised by diverse modes of coordination of tetrahydroborate ligands (η^1-, η^2- and η^3-BH_4, various types of BH_4 bridges between neutral species); complexes with BH_4 ligands of different denticities at one metal atom are also known. Most of complexes containing these metals in the oxidation states +3 and +4 comply with the principle of the maximum occupancy of the metal coordination sphere. The known tetrahydroborates of these metals possess clear-cut fluxionality (the protons of the BH_4 group are equivalent on the NMR time scale). Only for the complex $[Ti(CO)_4(\eta^3\text{-}BH_4)]^-[K(18C6]^+$, were the signals of the terminal and bridging protons of η^3-BH_4 distinguished in low-temperature NMR spectra.

The structures of alkali and alkaline earth metal tetrahydroborates have not been adequately studied. As indicated by the available data, characteristic features of these compounds include fluxionality, diversity of the modes of coordinations of tetrahydroborate ligands to metals, formation of BH_4 bridges between neutral molecular units; the principle of the maximum occupancy of the coordination sphere is often violated.

The structural chemistry of Group I and V–VIII transition metal tetrahydroborates is much less plentiful than that for the Group III and IV transition metals; the range of stabilising ligands is more limited; no complexes with η^3-BH_4 groups or with BH_4

bridges between neutral molecular units have been found. The principle of the maximum occupancy of the coordination sphere is not obeyed for these compounds.

In the complexes of Group I and V–VIII transition metals, BH_4 groups tend to be coordinated as mono- and bidentate ligands. Monodentate coordination is found only when the coordination sphere contains bulky ligands having strong electron-donating properties (phosphines, macrocyclic compounds), *i.e*. it is a forced type of coordination. The factors inducing the formation of complexes of these metals with mono- and bidentate coordination of the BH_4 ligands are not entirely clear yet. Whereas alkali, alkaline earth and rare earth metals and uranium tend to form polynuclear complexes due to tetrahydroborate bridges between neutral mononuclear molecules, in the case of Group I and V–VIII metals, the BH_4 bridges connect either cationic species or metal atoms bound into a cluster and located close to one another.

Tetrahydroborates of Group V–VIII transition metals possess higher stereochemical rigidities than complexes of Group IA, IIA, IIIB and IVB metals. For many of them, separate signals for terminal and bridging protons of mono- and bidentate BH_4 groups can be detected in low-temperature NMR spectra. In some of the compounds considered, the exchange of terminal and bridging protons does not proceed at a noticeable rate even at room or higher temperature. In some cases, bridging protons give rise to two separate NMR signals and the exchange of non-equivalent bridging protons with terminal protons occurs at different rates.

The absence of a trend for the maximum occupancy of the coordination sphere, the low coordination numbers and an increase in the stereochemical rigidity indicate that the degree of covalence of the $M-BH_4$ bond in Group V–VIII metal tetrahydroborates is higher than that in the Group IA, IIA, IIIB and IVB metal complexes.

Neither resorting to the views on the three-centre two-electron M–H–B bond, widely employed now, nor allowing for steric factors can substantiate in the general case the observed structures and some physical and chemical properties of tetrahydroborate complexes.

Analysis of the experimental data presented above led to the assumption that the crucial factor determining the differences in the structures and the dynamic properties of transition metal tetrahydroborate complexes is the electron configuration of their central ions, which is d^0 (d^1) for most of the Group III and IV metal compounds considered or d^n ($n = 2-10$) for Group I and V–VIII metal complexes. High coordination numbers, the trend for the maximum occupancy of the coordination sphere and fluxionality of the tetrahydroborates of Group IA, IIA, IIIB and IVB metals indicate that the $M-BH_4$ bonds in these compounds are mostly ionic. The fluxional behaviour of these compounds is apparently related to the fact that the spherically symmetrical electron shell of d^0 ions does not create barriers to free rotation of the BH_4^- anion in the metal coordination sphere. In the complexes with central d^n ions ($n = 2-8$), the mutual repulsion of the non-bonding *d*-electrons and coordinated BH_4^- anions destabilises the η^3-coordination of the BH_4 groups, which makes the most probable rearrangement pathway ($\eta^2-\eta^3-\eta^{2\prime}$) energetically less favourable and results in an increase of the stereochemical rigidity of complexes of Group V–VIII metals. In addition, this factor prevents the formation of tetrahydroborate bridges between neutral mononuclear molecules in d^n-metal tetrahydroborates ($n = 2-8$). Complexes with central d^{10} ions, possessing completely filled *d*-electron shells, occupy an intermediate position — there are no complexes with η^3-groups among them but stereochemically rigid complexes have not been found either.

The similarity of the structural and dynamic properties of tetraborate complexes formed by *f* elements and those with central d^0 ions (η^3-coordination, fluxional behaviour and the trend for maximum occupancy of the metal coordination sphere) leads to the conclusion that *f* electrons do not influence the properties of tetrahydroborate complexes as significantly as outer *d* electrons and they apparently do not participate in the formation of bonds of the central atom with the BH_4 ligand.

The data considered above provide information not only on the dependence of the structural and dynamic properties of the tetrahydroborate ligand on the electronic configuration of the central atom but also on the dependence of the coordination and, correspondingly, catalytic properties of the central atom on the structure of its outer electron shell.

Since the tetrahydroborate anion is isoelectronic with the methane molecule, tetrahydroborates can be regarded as models of some steps of C–H bond activation in saturated hydrocarbons.[3] It is noteworthy in this connection that the sharp difference between the coordination (and, hence, catalytic) properties of the complexes with central d^0 and d^n ions ($n = 2-10$) is also manifested in many systems related to the transformations of hydrocarbon ligands. Thus activation of methane and cyclometallation reactions with participation of d^0-ion complexes follow a mechanism which includes a multicentre transition state,[246] whereas activation of C–H bonds involving complexes with central d^n ions often proceeds according to an oxidative addition mechanism, similar to the exchange of hydride ligands and bridging hydrogen atoms in $OsH_3(BH_4)(PPr^i_3)_2$.[10]

It is also known that transition metal metallocene complexes with central d^0 ions act, under certain conditions, as active catalysts for polymerisation of α-olefins according to the so-called metallocene catalysis mechanism.[247] Similar complexes with d^n ions do not exhibit pronounced catalytic activity under the same conditions; the catalysts of α-olefin polymerisation based on d^n ions have a different composition, 'work' under different conditions and by a different mechanism.[248] By analogy with the BH_4 ligand, hydrocarbon ligands might possess different stereochemical rigidities and different denticities in the coordination with d^0 or d^n ions.

Further studies of structural and dynamic properties of the tetrahydroborate complexes with central d^0 and d^n ions are needed to understand the nature of the metal–ligand bond in these complexes. They are also required for development of the general views on the fluxional behaviour, for more extensive investigations of the dependence of the coordination and catalytic properties of metals on the electronic structures of their atoms and for modelling of the transition states in hydrocarbon activation processes.

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