TABLE III

VISIBLE–ULTRAVIOLET SPECTRA OF TITANOCENE COMPLEXES

Complex	Absorption maxima, kK[a]
$(C_5H_5)_2Ti(NCS)_2$	30.4 sh (9150), 29.2 (9470), 22.8 (9930), 18.2 sh (247)
$(C_5H_5)_2Ti(NCSe)_2$	30.9 (8230), 23.2 (6480), 20.9 (7260)
$(C_5H_5)_2Ti(OCN)_2$	30.8 (3850), 26.5 (3910), 20.3 (282)
$(C_5H_5)_2TiCl_2$	30.9 (3750), 25.7 (2240), 19.2 (430)

[a] Molar absorptivity shown in parentheses.

plexes of metals having high formal oxidation states, *e.g.*: $Nb(NCS)_6^{2-}$, 2035 cm^{-1}; $Nb(NCS)_6^{-}$, 1954, 1911 cm^{-1}.[14]

All of the cyanate complexes previously reported[5,15–20] have been found to be N bonded, the frequency shifts of their infrared bands, relative to those of the free ion, following the patterns exhibited by isothiocyanates and isoselenocyanates. Although the data shown in Table II for the titanocene–cyanate complex (also see Figure 1) are not as conclusive as those shown for its higher homologs, the absence of a C–O stretching band in the N-bonded range, the lower frequency NCO bending vibration, and the pronounced increase in the C–N stretching frequency all serve to indicate that the cyanate groups are O bonded. The similarity of the integrated absorption intensity of the C–N stretching band to the values exhibited by known isocyanate complexes (Table II) may be due to the small difference in mass between the nitrogen and oxygen atoms.

Coutts and Wailes[19] have recently reported the preparation of the corresponding titanium(III) complex, $(C_5H_5)_2TiNCO$. They concluded, on the basis of mass spectral data and the C–N stretching frequency of the complex (2175 cm^{-1}), that the cyanate group is N bonded. This represents, when compared with the $(C_5H_5)_2Ti(OCN)_2$ complex prepared in this study, a second example of the sensitivity of the bonding mode of an ambidentate ligand to the oxidation state of the metal to which it is coordinated. Both this example and the Cu^{I}–SCN and Cu^{II}–NCS N-heterocyclic amine complexes previously reported[21] exhibit a trend which is opposite to that predicted by Jørgensen,[22] namely, that the class b[23] or soft-acid[24] character of a metal should increase as its oxidation state increases, owing to increasing covalency in the bonds. The Ti–NCS, Ti–NCSe, and Ti–OCN bonding pattern exhibited by the $(C_5H_5)_2Ti^{2+}$ moiety is precisely that which would be expected for a hard acid and follows that previously elucidated by Rivest[25] for $TiCl_4$; *i.e.*, $Ti(NH_2CSNH_2)_2Cl_4$ contains N-bonded thiourea ligands, but, in $Ti(OC(NH_2)_2)Cl_4$, the urea groups are O bonded.

Extensions of this work to other ambidentate ligands and cyclopentadienyl complexes are in progress.

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[14] T. M. Brown and G. F. Knox, *J. Am. Chem. Soc.*, **89**, 5296 (1967).

[15] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 2790 (1964), 1286 (1965), and references contained therein.

[16] S. M. Nelson, *Proc. Chem. Soc.*, 372 (1961).

[17] M. Schafer and C. Curran, *Inorg. Chem.*, **4**, 623 (1965).

[18] S. M. Nelson and T. M. Shepherd, *ibid.*, **4**, 813 (1965).

[19] R. Coutts and P. C. Wailes, *Inorg. Nucl. Chem. Letters*, **3**, 1 (1967).

[20] A. H. Norbury and A. I. P. Sinha, *ibid.*, **3**, 355 (1967); *J. Chem. Soc. A*, 1598 (1968).

[21] R. H. Toeniskoetter and S. Solomon, *Inorg. Chem.*, **7**, 617 (1968).

[22] C. K. Jørgensen, *ibid.*, **3**, 1201 (1964).

[23] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

[24] R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

[25] R. Rivest, *Can. J. Chem.*, **40**, 2234 (1962).

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Hydrogen Bonding in Dimethylboric Acid

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Dimethylboric acid, $(CH_3)_2BOH$, was first prepared by Schlesinger and Walker.[1] The Trouton constant was later found to be 29.7, indicating some degree of association in the liquid phase.[2] The present study was undertaken to determine whether the association is of a monomer–dimer type or involves higher polymers, and, further, whether association takes place through hydrogen bonding or by boron–oxygen coordination.

Experimental Section

A high-vacuum apparatus of conventional design was used. Vapor pressure measurements were carried out in a tensimeter[3] attached to the vacuum system. Infrared spectra were measured using a Perkin-Elmer Model 421 grating spectrometer. For the solution spectrum, a 5–10% solution in carbon tetrachloride was prepared in the vacuum system and transferred by syringe to a standard 0.1-mm solution cell. The gas-phase spectrum was obtained using dimethylboric acid at 10 mm of pressure in a 5-cm cell with potassium bromide windows. A Varian A-60 spectrometer operating at 36° was used in the nmr studies; the variable-temperature investigation was carried out using a Varian HA-100 instrument. Nmr sample tubes were flamed lightly under vacuum and were sealed off after the components of solution had been distilled into them from the vacuum system.

Spectral grade solvents, dried over molecular sieves, were used in the infrared and nmr studies. Phillips pure grade *n*-butane was used in the tensimetric work; it was freed from water by slow distillation through a $-78°$ trap.

Dimethylboric acid was prepared by hydrolyzing purified dimethylboric anhydride (vapor pressure 148 mm at 0°)[4] with the stoichiometric quantity of water at room temperature. Distillation involving traps at -46, -78, and $-196°$ yielded the pure product (vapor pressure 36 mm at 0°; lit.[2] 36 mm at 0.4°) in the $-78°$ trap.

Results

The vapor pressure lowering in *n*-butane solutions of dimethylboric acid was investigated over a range of temperature and concentration. The results summarized in Table I establish that the system is complex,

[1] H. I. Schlesinger and A. O. Walker, *J. Am. Chem. Soc.*, **57**, 624 (1935).

[2] D. Ulmschneider and J. Goubeau, *Chem. Ber.*, **90**, 2733 (1957).

[3] A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 780 (1937).

[4] G. F. Lanthier and W. A. G. Graham, *Can. J. Chem.*, in press.

TABLE I

ASSOCIATION OF DIMETHYLBORIC ACID IN *n*-BUTANE[a]

Temp, °C	$(CH_3)_2BOH$,[b] cm³	*n*-C_4H_{10},[c] cm³	P_{soln}[d]	Deg of assocn
−63.5	2.6	63.2	28.62	7.1
	7.0	63.2	28.38	7.8
	12.9	63.4	27.90	6.5
	23.8	63.6	27.23	6.6
−45.3	2.5	48.0	92.02	3.4
	7.1	48.4	90.66	4.7
	11.8	48.8	88.91	4.7
	24.0	50.0	84.08	4.3
−36.0	2.5	33.3	155.49	4.0
	7.1	34.7	149.80	3.6
	11.8	35.8	145.40	3.7
	24.0	38.4	134.98	3.6

[a] Gas volumes are given at standard conditions. [b] Refers to monomeric species measured in the gas phase. [c] Refers to quantity in the solution, after correction for gaseous *n*-C_4H_{10} in the tensimeter over the solution. [d] Vapor pressures of pure *n*-butane at −63.5, −45.3, and −36.0° are 28.78, 93.45, and 158.38 mm, respectively.

with an average degree of association higher than 2 or 3. While the calculated values are subject to some uncertainty, particularly at low concentrations where the vapor pressure lowering is small, they permit a simple dimeric or trimeric system to be ruled out. As expected, the degree of association becomes smaller as the temperature increases.

The gas-phase infrared spectrum of dimethylboric acid has been reported by Ulmschneider and Goubeau.[5] The OH stretch previously reported at 3675 cm^{-1} resolves into a triplet at 3682, 3672, and 3662 cm^{-1} when run on an expanded scale with the higher resolution our grating instrument affords. The over-all half-width of this triplet absorption is *ca.* 25 cm^{-1}. The shape of the multiplet strongly resembles an incompletely resolved PQR band. This absorption is attributed to the monomeric species.

A 5–10% solution of the acid in carbon tetrachloride exhibited characteristic hydrogen-bonding effects. Two absorptions occur for the OH stretch: a sharp high-frequency absorption at 3635 cm^{-1} (half-width 27 cm^{-1}) and a broad absorption centered at 3375 cm^{-1} (half-width *ca.* 250 cm^{-1}). The latter, a smooth curve exhibiting no fine structure, is attributed to the hydrogen-bonded species.

The proton nmr spectrum of dimethylboric acid shows the expected two peaks. At 36°, we find the OH and CH_3 peaks at τ 1.28 and 9.64, respectively, for the neat liquid containing 1 mol % cyclohexane as internal standard. The shift of the CH_3 protons is essentially independent of concentration and temperature, in contrast to the OH shift, as discussed below. An earlier report[6] on the nmr of neat liquid dimethylboric acid gave τ 6.65 and 9.97 using a substitution method for calibration. The latter value is in reasonable agreement with our measurements when the difference in standardization is considered, but the τ 6.65 value for the OH proton is incompatible with the present work.

The concentration dependence of the chemical shift of the hydroxyl proton was studied over the range 1–99 mol % in cyclohexane solution. The shift varied markedly from 3.48 to 7.28 ppm downfield from cyclohexane, as shown graphically in Figure 1.

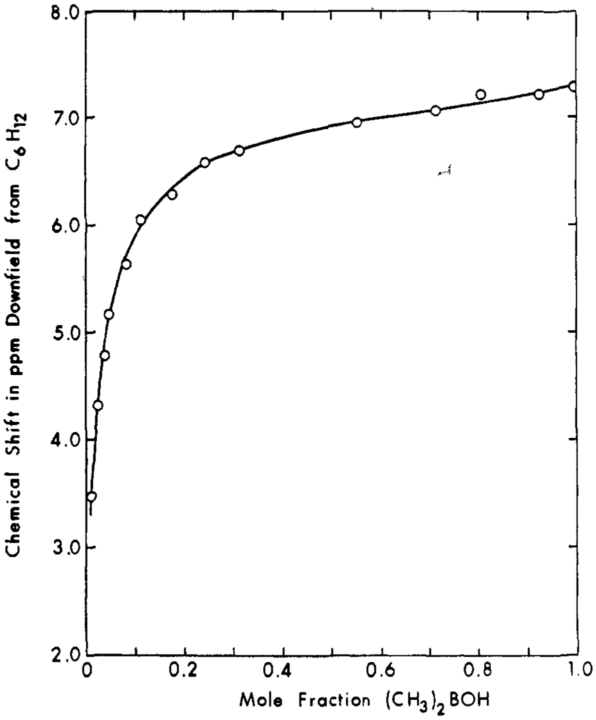

Figure 1.—Chemical shift of the OH proton resonance *vs.* the mole fraction of dimethylboric acid in cyclohexane at 36°.

The temperature dependence of the hydroxyl proton resonance was studied between −100 and 60°, using a 1 mol % solution of dimethylboric acid in methylcyclohexane, with results as shown in Figure 2. The limiting shift at high temperature was approached but not achieved, since further heating caused the sample to reflux and the signal was lost;[7] however, a value near 4.1 ppm downfield from tetramethylsilane would be a close estimate of the shift of pure monomer.

Discussion

The hydrolysis of dimethylboric anhydride may seem a devious route to dimethylboric acid, but it was used initially because of the availability of the anhydride from other work.[4] Since the anhydride was prepared[4] by partial hydrolysis of dimethylboron chloride, the method adopted here amounts to the hydrolysis of dimethylboron chloride in two stages

$$2(CH_3)_2BCl + H_2O = (CH_3)_2BOB(CH_3)_2 + 2HCl$$
$$(CH_3)_2BOB(CH_3)_2 + H_2O = 2(CH_3)_2BOH$$

This procedure is preferred in our experience to a one-step hydrolysis of dimethylboron chloride because the anhydride is more conveniently separated from im-

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(5) D. Ulmschneider and J. Goubeau, *Z. Physik. Chem.* (Frankfurt), **14**, 56 (1958).

(6) J. E. De Moor and G. P. Van der Kelen, *J. Organometal. Chem.* (Amsterdam), **6**, 235 (1966).

(7) Following the suggestion of a referee, an nmr tube was filled to about 1 atm with nitrogen. In this case, also, the signal was lost at elevated temperature.

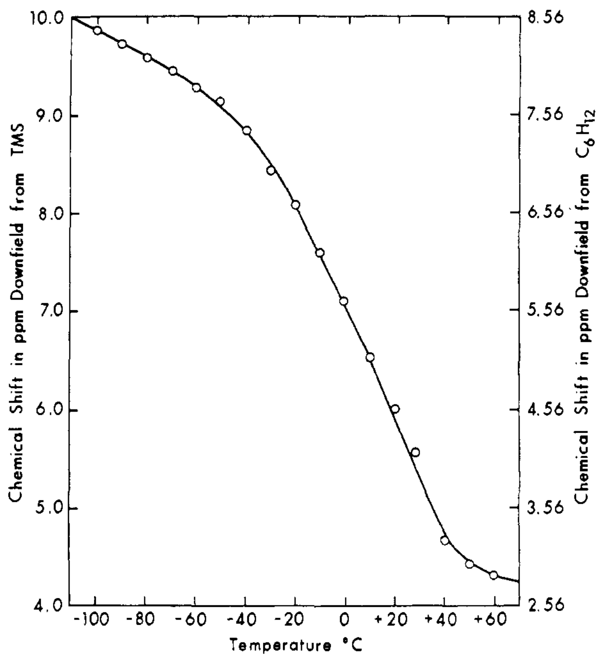

Figure 2.—Chemical shift of the OH proton resonance *vs.* temperature for a 1 mol % solution of dimethylboric acid in methylcyclohexane. Shifts relative to cyclohexane are calculated by subtracting 1.44 ppm from the chemical shift relative to tetramethylsilane (TMS).

purities, such as methylboric anhydride, than is dimethylboric acid from methylboric acid. The purification of dimethylboron chloride is also tedious.[4]

The broad OH stretching band in carbon tetrachloride and the concentration and temperature dependence of the hydroxyl proton chemical shift are typical for hydrogen-bonded protons. No attempt has been made to calculate the bond energy from the temperature dependence of the nmr spectrum, since the system involves several species in unknown concentrations. Further, extrapolation to obtain the maximum downfield shift of the hydrogen-bonded proton is somewhat uncertain (see Figure 2).

It is of interest to examine the present results in terms of a correlation proposed by Ferraro and Peppard;[8] these authors found a linear relation between the chemical shift of the hydroxyl proton in the region of "minor bond breaking" (*i.e.*, the relatively flat portion of Figure 1 at higher concentration) and the hydrogen-bond energy. A similar relation was noted between the bond energy and the difference in the infrared stretching frequencies of free and hydrogen-bonded OH groups.[8] Using this correlation, our value of *ca.* 7.3 ppm downfield from cyclohexane (8.7 ppm from tetramethylsilane) for the chemical shift of the hydroxyl proton in the region of minor bond breaking corresponds to a hydrogen-bond energy of 4.6 kcal. Furthermore, the value of 260 cm^{-1} obtained by subtracting the frequency of the bonded OH from the frequency of the free OH corresponds to an energy of 4.8 kcal. The good agreement between these two values leads us to place some confidence in the values obtained.

It is of interest to note that the shift of the hydroxyl proton of the monomer, *ca.* 4.3 ppm downfield from tetramethylsilane, occurs at a much lower field than that of the monomeric proton in ethanol, 0.76 ppm downfield.[9] This would indicate decreased shielding of the hydroxyl proton in dimethylboric acid, which is in keeping with the expected lowering of the electron density on the oxygen atom caused by the acceptor capability of the boron atom. Oxygen–boron back-donation would also account for the failure to observe any indication of intermolecular coordination; this is not unexpected, however, since methoxydimethylboron is not associated[10] despite the electron-releasing methyl group on oxygen.

Evidence for oxygen–boron π bonding, in terms of hindered rotation about the boron–oxygen bond, has recently been provided;[11] the splitting of the B-methyl resonance in methoxydimethylboron at −44° was attributed to this effect. Splitting of the methylboron resonance in dimethylboric acid was not observed down to −100°, presumably because very rapid hydrogen-bond breaking and forming averages out the environments of the B-methyl groups, irrespective of hindered rotation about the boron bond.

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[8] J. R. Ferraro and D. F. Peppard, *J. Phys. Chem.*, **67**, 2639 (1963).

[9] This value is derived from the work of E. D. Becker, U. Liddel, and J. N. Shoolery, *J. Mol. Spectry.*, **2**, 1 (1958), on the assumption that the central peak of the CH_3 triplet is 8.83 ppm downfield from tetramethylsilane.

[10] G. E. Coates, *J. Chem. Soc.*, 3481 (1950); A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

[11] G. F. Lanthier and W. A. G. Graham, *Chem. Commun.*, 715 (1968).

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Mössbauer Spectroscopy of Organometallic Compounds: $Fe(C_2B_9H_{11})_2^-$ and $(\pi\text{-}C_5H_5)Fe(C_2B_9H_{11})$

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The recent publication of a detailed analysis of the nqr resonance in $Cs(1,2\text{-}C_2B_9H_{11})_2Co$ and the comparison of the bonding in this carbollide with ferrocene and related molecules by Harris[1] prompt us to describe more fully the Mössbauer results referred to in that paper.

Experimental Section

Samples of $(CH_3)_4N[Fe(C_2B_9H_{11})_2]$ and $(C_5H_5)Fe(C_2B_9H_{11})$ were generously made available to us by Dr. P. Wegner and used

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[1] C. B. Harris, *Inorg. Chem.*, **7**, 1517 (1968).