molecules or bipyridine complexes with transition metals which impose a square-planar or octahedral configuration,[16] the central mediocyclic ring affords sufficient flexibilty to permit the nitrogen atoms access to the metal ion and to permit adequate avoidance of the terminal methyl substituents. Removal of these methyl substituents will probably make only a minor contribution to the ability of **5a** to complex Cu(II) ions, as based on their minimal interaction in complex **6b**.

Contrary to the lack of terminal group participation herein demonstrated, in a series of palladium(II) complexes of pyridine- and pyrazine-based ligands, we have observed that the terminal methyl groups have a tremendous effect on the mode of complexation.[17] Further work is in progress to delineate the effect(s) of terminal substituents in complex formation.

Registry No. 1, 83478-63-1; 2, 83478-64-2; 3, 82740-64-5; **4a**, 83478-65-3; **4b**, 83478-66-4; **5a**, 83478-67-5; **5b**, 83478-68-6; **6a**, 83478-70-0; **6b**, 83478-73-3; 6-methyl-2,2'-bipyridine, 56100-22-2.

Supplementary Material Available: Details of data collection and refinement for complex **6b** and tables of anisotropic thermal parameters, coordinates of hydrogen atoms, bond distances, bond angles, and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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Comments on the Formation of Bis(catecholato)borates. Potassium Bis(4-methylcatecholato)borate(III)

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Boric acid, $B(OH)_3$, is capable of forming complexes with bidentate chelating ligands according to eq 1 and 2. Ligands

$$\text{(1)}$$

$$\text{(2)}$$
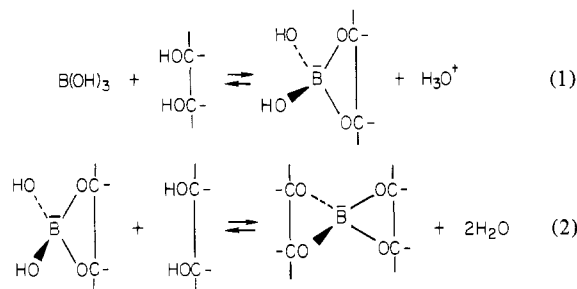
that undergo this type of reaction include polyols,[2-5] 1,2-benzenediols,[2,3,6,7] and α-hydroxy carboxylic acids.[8,9] While

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the existence of bis complexes has been generally accepted for polyols and α-hydroxy carboxylic acids, there has been considerable discussion over the years as to whether bis complexes of catechol and substituted catechols exist in aqueous solution to any appreciable extent. Although salts of bis(catecholato)borates can be isolated from aqueous solution,[3,10] reactant concentrations are generally quite high. Much of our recent work in the area has concerned the mechanism of formation of 1:1 complexes.[11,12] In the course of those studies, the complexation of boric acid with catechol and substituted catechols was investigated. Our kinetic and thermodynamic study of such reactions supports the contention that in acidic solution in which reactant concentrations are ≤ 0.05 M only 1:1 complexes are formed. However, in the case of 4-methylcatechol, we have isolated a white solid from slightly basic aqueous solution. The salt is potassium bis(4-methylcatecholato)borate(III). The present paper concerns the characterization and properties of that salt and a discussion of equilibria in boric acid systems of this type.

Experimental Section

Reactants were used as described previously.[12] The white solid reaction product was isolated from slightly basic aqueous solution ($\mu = 0.1$ M (KNO_3)) in the course of a pH titration. Elemental analysis is consistent with $K[(CH_3C_6H_3O_2)_2B]$. The salt melts at a temperature greater than 355 °C and is soluble in ethanol (with discoloration indicating ligand oxidation), THF, and $(CH_3)_2SO$. Infrared spectra were taken in KBr and Nujol on a Beckman 18A IR spectrometer; proton NMR spectra were taken in $(CD_3)_2SO$ on a Varian A-60.

Results

Although the vibrational spectra of complexes of this type have recently been analyzed,[5,9] only one spectral feature is of fundamental importance for our purposes. There is *no* O–H stretch in the infrared spectrum. Hence, there is no 1:1 complex present. The proton NMR spectrum is also consistent only with 1:2 complex formation. Two proton resonances occur, the peak integration showing the expected 1:1 ratio of aromatic to methyl protons with normal chemical shifts for such protons. Also of interest is the fact that the anion, $(CH_3C_6H_3O_2)_2B^-$, is stable in $(CH_3)_2SO$.

Discussion

The surprising aspect of the isolation of $K[(CH_3C_6H_3O_2)_2B]$ under our experimental conditions is that it precipitates from a solution in which the concentration of $(CH_3C_6H_3O_2)_2B^-$ must be very small. This result prompted an examination of the equilibria in boric acid systems. While such equilibria are conveniently studied by pH titration methods,[2-4,6,8,11,12] many other experimental techniques have been used. These include infrared[9] and Raman[5] spectroscopy, visible spectroscopy,[13] ^{13}C NMR,[14] ^{11}B NMR,[7] and ORD.[15]

The existence of equilibria as shown in eq 1 and 2 for α-hydroxy carboxylic acids has been generally accepted since the early work of Vermaas.[8] Extensive studies on borate/polyol complexes[2] have shown that these ligands also form complexes of both 1:1 and 1:2 stoichiometry. Equilibria involving catechol and substituted catechols have proved more problematic, with some authors[12-14] (ourselves included) finding only 1:1 complexes, some proposing both 1:1 and 1:2

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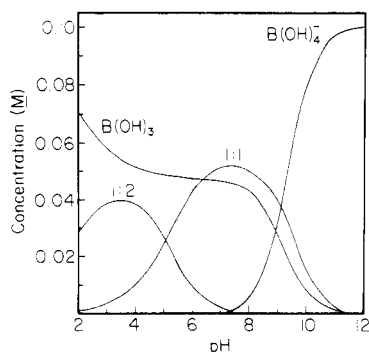(11) Babcock, L.; Pizer, R. *Inorg. Chem.* **1980**, *19*, 56.
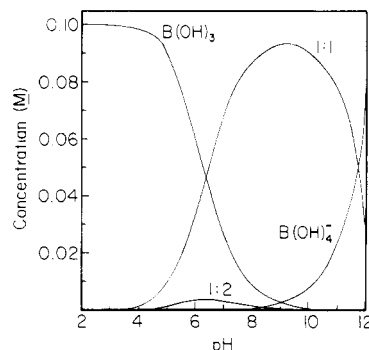(12) Pizer, R.; Babcock, L. *Inorg. Chem.* **1977**, *16*, 1677.
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Figure 1. Distribution diagram for the $B(OH)_3/\alpha$-hydroxyisobutyric acid system, calculated with 0.10 M concentration for each reactant.

Figure 2. Distribution diagram for the $B(OH)_3$/catechol system, calculated with 0.10 M concentration for each reactant.

Figure 3. Distribution diagram for the $B(OH)_3$/glycerol system, calculated with 0.10 M concentration for each reactant.

complexes,[2,3,6,7] and others finding that it depends on the substituent.[6,16] One reason for the different results is that these several studies were carried out at very different acidities and reactant concentrations. Experimental difficulties are also encountered due to polyborate formation[17,18] and ligand oxidation. It has been shown recently[19] that polyborate ions are also capable of forming complexes.
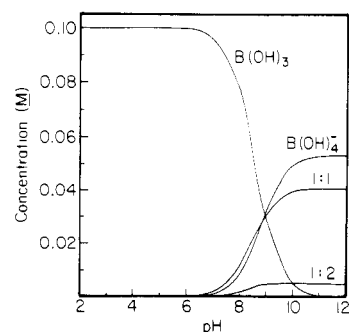
For an examination of these equilibria, reliable values of stability constants were taken from the literature for ligands varying widely in acidity. These values are collected in Table I. K_1 and K_2 refer to complex formation as indicated in eq 1 and 2. Since

$$[1:2]/[1:1] = K_2[H_2L] \qquad (3)$$

where H_2L refers to the unionized ligand, large concentrations of 1:2 complex will be formed only when *both* K_2 and the concentration of free H_2L are large.

Distribution diagrams were calculated for the first three of these systems (Figures 1–3). The calculations were carried out with total concentrations of both boric acid and ligand of 0.10 M. Considered in the calculations are the two complexation steps and the acid dissociation constants of ligand and boric acid ($pK_a = 8.98$).[20] The polyols, glycerol and mannitol, are not appreciably ionized even at the highest pH values considered. There is no appreciable polymerization of boric acid at these concentrations.[17] Only the concentrations of boron-containing species are plotted.

These systems have several common features. In *all* cases, the ratio $[1:2]/[1:1]$ decreases with increasing pH (eq 3). For α-hydroxyisobutyric acid and mannitol, the ratio considerably exceeds unity in acidic media because K_2 is so large.[21] This

point is of considerable interest because the calculations are carried out at a formal concentration ratio of reactants of 1:1. Obviously, a large excess of ligand would favor formation of the bis complex, but even under these conditions, bis complex formation is predominant in acidic solution for these ligands.[22] The ratio decreases due to both complex formation and ionization of uncomplexed ligand. Although the ratio $[1:2]/[1:1]$ decreases with increasing pH, the total concentration of complex increases with increasing pH in acidic media. For α-hydroxyisobutyric acid and catechol, the total complex concentrations go through maxima near pH 7 and pH 9, respectively. The decrease at higher pH values is primarily due to the ionization of uncomplexed ligand. Glycerol does not undergo appreciable ionization, and the total concentration of complex levels off at a maximum value in basic solution.

Despite the apparent differences in the three distribution diagrams, each system involves exactly the same equilibria. Differences are due only to the magnitudes of the various equilibrium constants. In the case of catechol, three factors are significant with respect to the low concentration of 1:2 complex. K_2 is low, K_1'/K_2 is large (see below), and the ligand is reasonably acidic.

Several studies of boric acid/catechol systems will be examined on the basis of the preceding discussion. First, it is interesting to point out that various determinations of K_1 for the boric acid/catechol system[2,6,7,12] and the boric acid/4-nitrocatechol system[12,13] agree within experimental error. However, only 1:1 formation was observed in two cases[12,13] while bis complex formation was indicated by others.[2,6,7] Our studies were carried out in dilute acidic solution.[12] In the study[13] of Skarp et al. reactant concentrations were even lower. If the stability constants of Antikainen[6] are taken as representative, bis complex formation would be minimal in both cases under experimental conditions. Pasdeloup's ^{13}C NMR study[14] was carried out at much higher boric acid (0.8 M) and catechol (0.4 M) concentrations at pH 6. The experiment revealed only 1:1 complex formation within experimental error, and this is consistent with K_1 and K_2 (Table I). The ^{11}B NMR study[7] of Yoshino and co-workers involved reactant concentrations as high as 1.0 M. This study showed an increase in

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(21) For mannitol under the same conditions at pH 6, $[1:2] = 2.2 \times 10^{-2}$ M and $[1:1] = 2.7 \times 10^{-3}$ M. Mannitol has been a difficult system, but an analysis by Knoeck and Taylor[4] of a number of studies of mannitol complexation shows that the various published results, despite seeming differences, are consistent with eq 1 and 2. However, Edwards[3] has made the point that ligands with four or more hydroxyl groups may bind more than one borate. From his estimated values of equilibrium constants for similar reactions, it can be concluded that such complexes are not important in acidic solution at the reactant concentrations considered here. However, in basic solution such equilibria would have to be considered. For this reason, a complete distribution diagram for this system is not presented here. It should also be noted that $[1:2]/[1:1]$ for both glycerol and catechol could exceed unity at higher reactant concentrations in acidic solution.
(22) An examination of this problem as it relates to the determination of stability constants is given in ref 4.

Table I. Stability Constants for Boric Acid Complexation with Four Ligands

ligand	K_{a1}, K_{a2}	K_1	K_2	K_1'/K_2[e]
α-hydroxy-isobutyric acid[f]	1.4×10^{-4}	3.3×10^{-3}	7.0×10^2	4.7×10^3
catechol	5.4×10^{-10} 3.2×10^{-12}[a]	9.8×10^{-6}[b]	1.9[b]	4.9×10^3
glycerol[g]		1.7×10^{-8}	2.6	6.2
mannitol	3.2×10^{-14}[c]	6.5×10^{-7}[d]	1.5×10^{2}[d]	4.1

[a] Reference 12. [b] Reference 6. [c] Thamsen, J. *Acta Chem. Scand.* **1952**, *6*, 270. [d] Reference 4. [e] $K_1' = K_1/K_a(B(OH)_3)$. [f] Reference 8. [g] Reference 2.

[1:2] as the pH was lowered from 11 to 6. This is consistent with Figure 2. All of the studies cited are correct in their conclusions. In the cases where bis complexes were not observed within experimental error, the reaction conditions were either too acidic[12] or too basic[23] or the reactant concentrations were too low[13] or were in the wrong proportion for bis complex formation to be seen.[14] Our isolation of a salt of a bis complex simply reflects a low solubility product constant. The salt precipitates under conditions where the concentration of anion is too low to detect by pH titration methods within experimental error.

A final point to consider is the ratio of the stability constants. As written, K_1 and K_2 cannot be directly compared. However, if eq 1 is rewritten to involve reaction of tetrahedral borate, a direct comparison can be made. Written this way, $K_1' = K_1/K_a(B(OH)_3)$. The appropriate ratio, K_1'/K_2, is included in Table I. From a purely statistical point of view $K_1'/K_2 = 12$. Obviously, the experimental ratio is close to the statistical ratio only for polyols, although it should be noted that even for polyols the ratio varies considerably.[3–5] The very high values for α-hydroxyisobutyric acid and catechol suggest that, in these cases at least, a bound ligand has a profound effect on the second complexation step.

Experimental ratios considerably *less* than those predicted from statistics have been observed in oxyanion systems with catechol, and a very interesting mechanistic explanation has been offered to account for the result.[24] This is of particular interest to us since we have previously pointed out[12] mechanistic similarities in the formation of 1:1 complexes with catechol of boron acids and oxyanions. The mechanistic reason for the very great difference in the formation of bis complexes is an open question under active investigation in our laboratory.

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Cis and Trans Ammonia Labilization in the Thermal Aquation of [Cr(NH₃)₅F]²⁺

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The complex $[Cr(NH_3)_5F]^{2+}$ has been the subject of several kinetic and photochemical studies,[1–4] and it is now well es-

Table I

[H⁺], M	$10^6 k_{F^-}$, s⁻¹ [c]	$10^6 k_{F^-}$, s⁻¹ [a]	$10^6 k_{NH_3}$, s⁻¹ [c]	% trans[b]
0.01 (HClO₄)	0.55 (2)	2.13	6.1 (3)[d]	23
0.10 (HClO₄)	1.1 (1)	2.39	6.9 (2)[d]	23
1.0 (HClO₄)	8.5 (2)	5.00	7.8 (2)[d]	
0.10 (HCl)	0.76 (1)		3.8 (1)	27
1.0 (HCl)	8.3 (1)		3.0 (1)	27

[a] Calculated from the results of ref 2. [b] % trans refers to the $[Cr(NH_3)_4H_2OF]^{2+}$ product; analysis was by ion-exchange chromatography with estimated uncertainty ±5%. [c] Number of determinations in parentheses. [d] The calculated k_{NH_3} is 7.7×10^{-6} s⁻¹.

tablished that, except in strong acid, the molecule predominantly aquates ammonia, both thermally and photochemically. Whereas the photochemical reaction has been investigated with regard to the isomeric nature of the $[Cr(NH_3)_4H_2OF]^{2+}$ product, showing that it is 85% cis and 15% trans, no such study appears to have been carried out for the thermal reaction. Data on this point would be of interest as, if stereoretentitivy of aquation is assumed, they indicate the extent of cis vs. trans labilization of the ammonia ligands by the fluoride ligand.

Al-Shatti and co-workers[2] have summarized the evidence that a number of chromium(III) pentaammines with ligands containing uncoordinated oxygen atoms exhibit significant cis labilization of ammonia. This phenomenon has been ascribed to one of (i) direct coordination of oxygen to the metal to form a seven-coordinate intermediate, (ii) H bonding to an adjacent coordinated ammonia, interpreted variously as causing weakening[5] or strengthening[6] of the Cr–N bond, or (iii) H bonding to an adjacent coordinated ammonia to give an intramolecular conjugate base effect, leading to the loss of a different ammonia ligand. They further note that the effective cis-labilizing ligands appear to be those capable of forming seven-coordinate intermediates and that labilization by hydroxide and fluoride presumably would occur via ligand to metal π donation. Consequently, the question of whether cis or trans labilization occurs with fluoride is of some interest and was convenient for us to investigate in light of our experience of such analyses.[3]

The compound $[Cr(NH_3)_5F](ClO_4)_2$ was prepared and recrystallized as in the literature.[2] The thermal aquation of 1.0×10^{-2} M $[Cr(NH_3)_5F]^{2+}$ solutions was investigated in the dark at 50 °C in aqueous 1 M lithium perchlorate media at various acid concentrations in the range 1×10^{-2} M and to conversions in the range 10–20%. For the highest acid concentrations the use of hydrochloric acid was mandated, to avoid solubility problems. Rate constants for ammonia and fluoride aquation were determined by direct analysis for ammonia by coulometric titration[7] and for fluoride with a solid-state fluoride electrode, after isolation of the respective free ions with ion-exchange columns. The nature of the aquo products of ammonia loss was investigated by cation-exchange chromatography on a 20 cm × 8 mm column of Hamilton HC8X resin.

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