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A Boron Analogue of a Hydroxamic Acid: Synthesis, Characterization, and Behavior in Selected Chemical Systems

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The synthesis and characterization of the first boron hydroxamic acid, trimethylamine(*N-B*)boranecarbohydroxamic acid hydrochloride has been accomplished. The boranecarbohydroxamic acid was characterized by infrared, ^1H NMR, ^{11}B NMR, and mass spectroscopies and by its reaction with metal ions. Analytical data support the structure of this new compound as being $(CH_3)_3N\cdot BH_2C(O)NHOH\cdot HCl$ (**1**). The pK_a values, determined in 0.1 M $NaClO_4$ solution at 25 °C, were $pK_1 = 3.9$ and $pK_2 = 8.3$. The pK_2 value corresponds well with the pK_a values of organic hydroxamic acids. Formation constant data obtained in 0.125 M $NaClO_4$ at 25 °C for **1** with iron(III) show that the boron acid binds to iron(III) about as strongly as benzohydroxamic acid (log $\beta = 28.0$). The formation constants of **1** with nickel(II), cobalt(II), zinc(II), and copper(II) were also determined in 0.125 M $NaClO_4$ at 25 °C and are shown to follow both the Irving–Williams and Mellor–Malley order of stabilities.

Introduction

The synthesis of trimethylamine–carboxyborane, $(CH_3)_3N\cdot BH_2COOH$, the protonated boron analogue of the amino acid betaine, $(CH_3)_3N^+CH_2COO^-$, has been reported by Spielvogel.[1] Both $(CH_3)_3N\cdot BH_2COOH$ and its *N*-ethylcarbamoyl derivative $(CH_3)_3N\cdot BH_2C(O)NHC_2H_5$ have been shown to possess significant biological activity.[2,3] The difference between the carbon and boron analogues is reflected in pK_a values, the pK_a for trimethylamine–carboxyborane being 6 log units more basic than the corresponding value for betaine.[4] Although synthesis of several boron analogues of amino acids and more recently of acetylcholine has been accomplished,[5] no boron analogues of hydroxamic acids have been reported.

Hydroxamic acids are weak organic acids[6] with a wide variety of applications including use as antifungal agents, as pharmaceuticals, and in nuclear fuel processing.[7] One of the important characteristics of hydroxamic acids is their ability to form stable transition-metal complexes,[8] defining the basis for their usefulness as analytical reagents. The deep purple or red color of complexes of hydroxamic acids with the ferric ion serves as a fairly specific qualitative test for the hydroxamato group.[8] Because of the interest in boron analogues of amino acids and their biological activity and in consideration of the usefulness of hydroxamic acids, we have investigated the synthesis, characterization, and behavior in selected chemical systems of the first example of a boron analogue of a hydroxamic acid.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer on samples prepared as KBr disks. ^1H NMR spectra were obtained at 90 MHz with a JEOL FX90Q spectrometer, while ^{11}B NMR spectra were obtained at 32.1 MHz. ^{11}B NMR chemical shift measurements were obtained by the tube interchange technique using $(C_2H_5)_2OBF_3$ as a standard. UV–visible spectra were recorded on a Beckman Model 35 spectrophotometer. The mass spectrum was obtained with an LKB 2091 spectrometer operating at 70.1 eV. Melting points were determined on a Thomas Hoover capillary apparatus and are uncorrected. C, H, and N analyses were performed by M-H-W Laboratories, Phoenix, AZ. Job's method of continuous variation was used to establish the empirical composition of the boronecarbohydroxamic acid metal complexes with iron(III) and chromium(III).

Reagents and Solvents. All inorganic chemicals were analytical reagent grade and were used without further purification. Trimethylamine–cyanoborane, $(CH_3)_3N\cdot BH_2CN$,[9] triethyloxonium tetrafluoroborate, $(C_2H_5)_3OBF_4$,[10] and trimethylamine–carboxyborane, $(CH_3)_3N\cdot BH_2COOH$,[1] were prepared as reported in the literature. The intermediate product in the trimethylamine–carboxyborane synthesis, $(CH_3)_3N\cdot BH_2CN^+C_2H_5BF_4^-$, should be thoroughly dried under high vacuum as previously noted by Kemp.[11]

Determination of Dissociation Constants. The dissociation constants for $(CH_3)_3N\cdot BH_2C(O)NHOH\cdot HCl$ (**1**) were determined and calculated according to standard procedures, as were the formation constants of the metal complexes of **1**.[12]

Preparation of $(CH_3)_3N\cdot BH_2C(O)NHOH\cdot HCl$ (1). A solution of $NH_2OH\cdot HCl$ (0.75 g, 1.1 mmol) in water (10 mL) was added to a stirred aqueous solution of $(CH_3)_3N\cdot BH_2COOH$ (1.5 g, 1.3 mmol; 30 mL). The resulting solution was heated at 40–45 °C for 72 h, and the solvent was then removed by rotary evaporation. The white solid was washed with CH_2Cl_2 (2×20 mL) to remove excess $(CH_3)_3N\cdot BH_2COOH$ and dried under high vacuum for 24 h at ambient temperature. Recrystallization of this solid was not successful due to its extremely high solubility in water, insolubility in organic solvents, and instability in alcohols. However, the formulation $(CH_3)_3N\cdot BH_2C(O)NHOH\cdot HCl$ (**1**) is supported by reaction with iron(III) and chromium(III) and by physical and spectroscopic data: mp 108–110 °C dec; ^1H NMR (CD_3SOCD_3, $(CH_3)_4Si$) δ 2.68 (s, 9 H, $(CH_3)_3N$), 6.15 (br s, 2 H, NH, COH), 10.4 (br s, 1 H, OH); ^{11}B NMR (D_2O) δ −4.10 (t, BH_2, $J_{B-H} = 110$ Hz). Anal. Calcd for $C_4H_{13}BN_2O_2\cdot HCl$: C, 28.52; H, 8.38; N, 16.64. Found: C, 28.59; H, 10.78; N, 18.86. Anomalous elemental analyses have been reported for hydroxamic acids.[13] A sample of deuteriated boranecarbohydroxamic acid was prepared by stirring **1** in D_2O for 2 h and isolating the product as described above. Conductivity results indicated the presence of two ions due to the boranecarbohydroxamic acid cation and the chloride anion. A spectrophotometric test[14] for excess hydroxylamine in the boranecarbohydroxamic acid product indicated that there was no free hydroxylamine present. A qualitative test with silver nitrate confirmed the presence of chloride ion. A solution of $NaB(C_6H_5)_4$ (2.8 g, 8.3 mmol) in water (30 mL), added to a vigorously stirred solution of **1** (1.4 g, 8.3 mmol) in water (10 mL), immediately produced a white precipitate. The precipitate was filtered, washed first with hot water (2×25 mL) and then with ether (40 mL), and dried under high vacuum for 24 h to give a compound formulated as $(CH_3)_3N\cdot BH_2C(O)NHOH\cdot HB(C_6H_5)_4$ (3.4 g, 90%): mp 150–152 °C dec; IR (KBr disk) 3280 (NH), 3200 (OH), 3050, 3000 (CH), 2460 (BH), 1575 (amide I, C=C) cm^{-1}; ^1H NMR (CD_3COCD_3, $(CH_3)_4Si$) δ 2.70 (s, 9 H, $(CH_3)_3N$), 4.02 (br s, 1 H, NH), 4.59 (br s, 1 H, OH), 6.82 (br s, 1 H, COH), 7.02, 7.37 (m, 20 H, $B(C_6H_5)_4^-$); ^{11}B NMR (CD_3COCD_3) δ −4.18 (t, BH_2, J_{B-H} = 112 Hz), −6.76 (sh s, $B(C_6H_5)_4$).

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Preparation of Iron(III) and Chromium(III) Complexes. The iron(III) complex was prepared by reacting of 3 equiv of **1** (0.61 g, 3.6 mmol) and 1 equiv of $FeCl_3{\cdot}6H_2O$ (0.32 g, 1.2 mmol) in aqueous solution at pH 4.5, removing the solvent by rotary evaporation, and extracting the red solid with methanol. The methanolic solution was then concentrated by rotary evaporation to give the desired tris(boranecarbohydroxamato)iron(III) complex. The chromium(III) complex was synthesized by the reaction of 3 equiv of **1** with 1 equiv of $CrCl_3{\cdot}6H_2O$ in aqueous solution at pH 4. The resulting tris(boranecarbohydroxamato)chromium(III) complex was isolated in a manner identical with that for the iron(III) complex.

Results and Discussion

Boron Hydroxamic Acids. Synthesis and Characterization of Trimethylamine(*N*–*B*)boranecarbohydroxamic Acid Hydrochloride. The synthesis of the first example of a boron analogue of a hydroxamic acid, $(CH_3)_3N{\cdot}BH_2C(O)NHOH{\cdot}HCl$ (**1**), has been accomplished by the reaction shown in eq 1, which gives

$$(CH_3)_3N{\cdot}BH_2COOH(aq) + NH_2OH{\cdot}HCl(aq) \xrightarrow{\text{pH } 2} (CH_3)_3N{\cdot}BH_2C(O)NHOH{\cdot}HCl(aq) + H_2O \quad (1)$$

yields as high as 85%. The presence of the chloride ion in **1** was established by a qualitative test with silver nitrate. The boranecarbohydroxamic acid may be precipitated from aqueous solution as a tetraphenylborate salt. Infrared, proton NMR, and boron-11 NMR spectral data support the replacement of the chloride ion by the tetraphenylborate ion to give $(CH_3)_3N{\cdot}BH_2C(O)NHOH{\cdot}HB(C_6H_5)_4$. The reaction to form **1** was monitored by removing an aliquot at 24-h intervals and obtaining its ^{11}B NMR spectra. The results of this study revealed that the 1:2:1 triplet at −10.2 ppm, assigned to the BH_2^- moiety in $(CH_3)_3N{\cdot}BH_2COOH$,[1] gradually disappeared and a new triplet at −4.10 ppm gradually appeared, which was the only boron-containing species present after 72 h. This triplet is assigned to the $-BH_2^-$ moiety in $(CH_3)_3N{\cdot}BH_2C(O)NHOH{\cdot}HCl$ (**1**). The downfield shift of the $-BH_2^-$ resonance in **1** compared to that in $(CH_3)_3N{\cdot}BH_2COOH$ (−10.2 to −4.10 ppm) is consistent with the shift observed when one compares $(CH_3)_3N{\cdot}BH_2COOH$ with its *N*-ethylcarbamoyl derivative $(CH_3)_3N{\cdot}BH_2C(O)NHC_2H_5$ (−10.2 to −7.40 ppm), indicating that an amidic linkage is formed in each case.

As mentioned previously, only the triplet at −4.10 ppm due to the $-BH_2^-$ moiety in **1** was observed by ^{11}B NMR spectroscopy after 72 h of reaction time. Therefore, the reaction to produce **1** appears to go to an equilibrium that favors the product rather than to an equilibrium where only a small amount of **1** is present at any time. The latter situation is the case for the synthesis of acetohydroxamic acid from the reaction of aqueous acetic acid and hydroxylamine in aqueous acidic solution (eq 2).[15] In fact,

$$CH_3COOH + NH_2OH{\cdot}HCl \rightleftharpoons CH_3C(O)NHOH{\cdot}HCl + H_2O \quad (2)$$

on the basis of the high yield (85%) of the boranecarbohydroxamic acid, we conclude that the reverse reaction, the acid-catalyzed hydrolysis of acetohydroxamic acid (eq 2), does not occur to any appreciable extent for **1**. The reason the boranecarbohydroxamic acid preparatory reaction appears to have a high equilibrium constant is due to the fact that **1** is extremely stable in aqueous acidic solution. On the other hand, $CH_3C(O)NHOH{\cdot}HCl$ is not stable in aqueous acidic solution, and the equilibrium is favored in the direction of decomposition back to CH_3COOH and $NH_2OH{\cdot}HCl$.[15]

Infrared Spectrum of 1. The infrared spectrum of **1** exhibits absorption bands characteristic of O–H, N–H, B–H, amide I, amide II, and N–O stretching vibrations.[16-18] A hydrogen-bonded O–H stretching vibration for **1** is assigned to the strong shoulder at 3030 cm^{-1}, while the free hydroxyl stretching vibration is assigned to the strong and broad band at 3100 cm^{-1}. Upon deuteriation, these two O–H bands should disappear and move to new positions at lower wavenumber. An examination of the spectrum of the deuteriated boranecarbohydroxamic acid shows that the free O–H band at 3100 cm^{-1} moves to 2250 cm^{-1} and the associated O–H stretching band at 3030 cm^{-1} moves to 2165 cm^{-1} upon deuteriation. The ratio of each frequency to that of its deuteriated analogue is 1:1.4, as expected.[19]

Table I. Ionization Constants[a] of the Hydroxamate Hydroxyl Proton of Hydroxamic Acids[33]

hydroxamic acid	pK_a	hydroxamic acid	pK_a
formo	8.77	5-nitrosalicylo	6.89
aceto	9.02	phenylaceto	9.23
benzo	8.50	propeno	9.52
glycine	7.80	chloroaceto	8.52
D-lysine	8.11	isonicotino	7.94
salicylo	7.41	trimethylamine(*N*–*B*)-boranecarbo	8.30
nicotino	8.27		

[a] All pK_a's determined in water at 25 °C and μ = 0.1.

The strong band at 3190 cm^{-1} in the spectrum of **1** is assigned as the N–H stretching vibration, which moves to 2300 cm^{-1} on deuteriation.[20] The B–H stretching vibration is assigned to the strong, sharp band at 2450 cm^{-1}, which does not disappear upon deuteriation of **1**. This assignment is consistent with the range of frequencies observed for the B–H absorption band in the spectra of boron analogues of amino acids, $(CH_3)_xNH_{3-x}{\cdot}BH_2COOH$ (x = 0–3),[1,5a] and their *N*-ethylcarbamoyl derivatives,[3a] $(CH_3)_xNH_{3-x}{\cdot}BH_2C(O)NHC_2H_5$ (x = 0–3).

A particularly informative region in the spectrum of **1** is 1400–1650 cm^{-1}. The strong and broad band at 1600 cm^{-1} is assigned to an amide I band, consisting of contributions[21] from two possible resonance forms, i.e., $(CH_3)_3N{\cdot}BH_2C({=}O^+H)NHOH{\cdot}Cl^-$ and $(CH_3)_3N{\cdot}BH_2C(OH){=}N^+HOH{\cdot}Cl^-$. Two pieces of experimental data support this assignment: first, upon deuteriation the amide I band disappears and a new band appears at lower wavenumber (1475 cm^{-1}), and second, the amide I band shifts to higher wavenumber (1640 cm^{-1}) when **1** is dissolved in dimethyl sulfoxide. This behavior is characteristic of a carbonyl band.[20] In contrast, Spielvogel[16] has assigned a C=N stretching vibration to an absorption band that occurs at 1635 cm^{-1} in the infrared spectrum of the protonated boron *N*-ethylcarbamoyl derivative $(CH_3)_3N{\cdot}BH_2C(OH){=}N^+HC_2H_5{\cdot}Cl^-$, the structure of which has been elucidated by X-ray crystallography. On the basis of this crystal structure, Spielvogel has concluded that two resonance forms are possible for this compound, consisting primarily of the structure $(CH_3)_3N{\cdot}BH_2C(OH)N^+HC_2H_5{\cdot}Cl^-$, although the resonance form $(CH_3)_3N{\cdot}BH_2C({=}O^+H)NHC_2H_5{\cdot}Cl^-$ also contributes significantly.

The strong and sharp band at 1428 cm^{-1} in the spectrum of **1** is completely removed by deuteriation and is assigned as an amide II band, by analogy with secondary amides and various substituted benzohydroxamic acids.[19] Lastly, the N–O stretching vibration in the infrared spectra of organic hydroxamic acids usually appears as a weak band in the region 975–900 cm^{-1} and thus the weak band at 935 cm^{-1} in the spectrum of **1** is assigned to the N–O stretching vibration.[22]

Proton NMR. The ^1H NMR spectrum of **1** in DMSO-d_6 confirms the presence of the trimethylamine (s, 2.67 ppm) and hydroxamate hydroxyl groups (s, 10.6 pm). The position of the latter proton resonance is comparable to that observed in the ^1H NMR spectra of organic hydroxamic acids.[23] The exchange-

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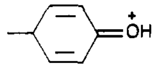
Table II. Formation Constants of Metal Boranecarbohydroxamate Complexes Determined at 25 °C

metal	log K_1	log K_2	log K_3	log K_1K_2	log $K_1K_2K_3$
Co(II)	9.96 ± 0.05	7.51 ± 0.02		17.47 ± 0.04	
Ni(II)	9.92 ± 0.05	7.67 ± 0.06		17.59 ± 0.04	
Cu(II)	10.53 ± 0.02	8.13 ± 0.01		18.66 ± 0.02	
Zn(II)	9.33 ± 0.01	6.81 ± 0.01		16.14 ± 0.01	
Fe(III)	11.86 ± 0.03	9.13 ± 0.04	7.01 ± 0.04		28.0 ± 0.06

broadened peak at 6.19 ppm, which is integrated for two protons, is assigned to the NH[23] and COH proton resonances. The assignment of the carbonyl oxygen as the site for protonation in **1** is consistent with infrared data. Moreover, the COH proton should be considerably less shielded than, for example, an alcohol OH proton (where $\delta = 2$–4) and the shift to lower field of the COH proton resonance is consistent with this observation. In fact, a phenolic proton resonance is also about 3 ppm to the low-field side of an aliphatic alcohol OH signal. This reduced shielding of the phenolic hydrogen has been interpreted[24] in terms of resonance forms of the type



This resonance form is also possible for **1**. In D_2O the trimethylamine group is observed, as is a peak at 4.70 ppm (HOD).

Mass Spectrum. The peaks and fragmentation processes observed (loss of NHOH, H_2O, and CO) are consistent with the structure of $(CH_3)_3N{\cdot}BH_2C(O)NHOH{\cdot}HCl$ (**1**) and are diagnostic of organic hydroxamic acids such as $C_6H_5C(O)NHOH$. A molecular (parent) ion peak was not observed.

Chemistry of Trimethylamine(*N*–*B*)boranecarbohydroxamic Acid Hydrochloride. Reactivity of the Boranecarbohydroxamic Acid in Acidic and Basic Solution. The ^{11}B NMR data for **1** supports the fact that electron density is being shifted from the boron nucleus since the $-BH_2^-$ resonance for **1** occurs at −4.10 ppm, a value considerably downfield from the $-BH_2^-$ resonance observed for $(CH_3)_3N{\cdot}BH_2COOH$ at −10.2 ppm. The electron density is being shifted from the boron nucleus to the carbonyl group, rendering the carbonyl carbon less electrophilic and stabilizing the boron analogue of the carbonyl-protonated form for **1**. In acidic solution the boron analogue of the carbonyl-protonated form is so kinetically inert that any significant buildup of the boron analogue of the nitrogen-protonated form is effectively blocked, with the result that **1** cannot hydrolyze via the acid-catalyzed pathway available to its organic counterparts.[25–27]

In contrast, we have observed that **1** will hydrolyze in basic solution. A study of the stability of **1** over the pH range 7–12 was performed by adding 0.2 M NaOH to an aqueous solution of **1** and then monitoring the change in the 1:2:1 triplet, assigned to the $-BH_2^-$ resonance. No change in the ^{11}B NMR spectrum occurs up to a pH of 9.5, at which point a large singlet at +9.44 ppm and another peak at −8.67 ppm appears in addition to the triplet at −4.10 ppm. At a pH of 12, the ^{11}B NMR spectrum consists only of the singlet at +9.44 ppm, assigned to boric acid,[28] and a triplet at −8.67 ppm, assigned to the $-BH_2^-$ resonance in $(CH_3)_3N{\cdot}BH_2CO_2^-Na^+$.[29]

These results are explained by considering the mechanism whereby organic hydroxamic acids hydrolyze in basic solution[30] to give a carboxylate. The appearance of the triplet at −8.67 ppm suggests that the mechanisms are similar enough for **1** and organic hydroxamic acids that they yield the same end products, $(CH_3)_3NBH_2CO_2^-$ and RCO_2^-, respectively. The difference found with the boron compound is that as the pH steadily increases, some of the B–H bonds hydrolyze, as evidenced by the formation of boric acid.

Reaction of 1 with Chromium(III) and Iron(III). The reaction of 3 equiv of **1** with 1 equiv of chromium(III) in aqueous solution at pH 4 results in the formation of a coordination complex, as evidenced by an immediate color change of the chromium(III) solution from bluish purple to dark green when **1** is added. The ^{11}B NMR spectrum of the complex in methanol shows a 1:2:1 triplet at −5.70 ppm, indicating that the $-BH_2^-$ moiety remains intact. In contrast, when uncomplexed **1** is dissolved in methanol, it rapidly decomposes, losing B–H in the process. The fact that the product of the reaction of **1** with chromium(III) is stable in methanol supports the notion that complexation of **1** has occurred. The application of Job's method to the dark green complex of chromium(III) and the boranecarbohydroxamic acid gives an empirical composition of 1:3 at pH 4.

The visible spectrum of the chromium(III) tris(boranecarbohydroxamic acid) complex in methanol is typical of that of an octahedral chromium(III) complex, consisting of two absorption bands centered at 410 nm ($^4A_{2g} \rightarrow {}^4T_{2g}$) and 610 nm ($^4A_{2g} \rightarrow {}^4T_{1g}$). The first ligand field band at 410 nm for the chromium(III) ion (d^3) corresponds to the 10*Dq* value and may be compared with similar values reported by Chatterjee[31] for chromium(III) tris(hydroxamic acid) compounds. The spectrochemical series of ligands obtained by comparison of 10*Dq* values indicates that **1** presents a stronger ligand field than the aromatic hydroxamic acids toward chromium(III). Attempts to isolate the chromium(III) tris(boranecarbohydroxamic acid) complex by recrystallization techniques were unsuccessful due to its extremely high solubility in water and alcohols.

The reactions of **1** with iron(III) in aqueous solution are similar to those of organic hydroxamic acids. In the presence of excess **1**, ferric iron develops a purple color (λ_{max} 500 nm) at pH 1.5, a red color (λ_{max} 485 nm) at pH 2.8, and a golden yellow color (λ_{max} 485 nm) at pH 4.5. This behavior with ferric iron is general for monohydroxamic acids[32] and indicates that complexes of varying ratios are formed at different hydrogen ion concentrations. However, the complexes of iron(III) with **1** are fully formed at the lower limit of each pH range compared to the pH at which complexes of iron(III) with organic hydroxamic acids are fully formed. This result indicates that, in the competition between hydrogen ions and ferric iron for the boranecarbohydroxamato ion, the formation of an iron(III) complex is favored. The empirical compositions of the 1:1, 2:1, and 3:1 complexes of **1** with iron(III) have been verified by using Job's method of continuous variation.

Infrared Spectra of Complexes of 1 with Iron(III) and Chromium(III). The infrared spectra of both the tris(boranecarbohydroxamato)iron(III) and chromium(III) complexes as compared to that of uncomplexed **1** shows two major differences that are indicative of complexation. The amide I stretching frequency for **1** is located at 1600 cm^{-1} but has shifted 10 cm^{-1} to lower frequency in the iron(III) complex. Complexation through the carbonyl oxygen of an organic hydroxamic acid usually causes a shift of the C═O stretching vibration to lower frequency. The magnitude of the shift observed for the carboxyl stretching frequency of organic hydroxamic acids upon coordination to a metal ion is normally in the range of 10–70 cm^{-1}, depending on the strength of the coordinate bond between the metal and the carbonyl oxygen.[18] However, this change is not substantial for the carbonyl stretching frequency of the tris(boranecarbo-

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hydroxamato)iron(III) and -chromium(III) complexes since the carbonyl oxygen can be considered complexed by H^+ as exemplified by one resonance form of **1**, i.e., $(CH_3)_3N\cdot BH_2C(=O^+\text{-}H)NHOH\cdot Cl^-$. The complexation to a +3 metal ion does not substantially affect the C=O stretching frequency since three boranecarbohydroxamato ligands are complexed to the metal.

The second difference between the spectrum of **1** and those of its iron(III) and chromium(III) complexes is the position and intensity of the N—O stretching vibration. The N—O stretching vibration for the hydroxamato group in **1** was assigned to the weak absorption at 935 cm^{-1}. Complexation should shift this N—O bond to higher frequency due to an increase in the $-N{=}O^-M^+$ contribution since the O–M bond formed is more ionic than the O—H bond that existed before coordination. A slight increase in intensity is also expected for this band due to coordination to the metal ion. The spectrum of each complex reveals a band of medium intensity at 950 cm^{-1}, which is assigned to the N—O stretching vibration. The weak absorption at 935 cm^{-1} due to uncomplexed **1** is absent.

Acid Dissociation Constants and Formation Constants. The acid dissociation constants of **1** were measured so that information concerning the coordinating ability of this novel ligand could be obtained. The pK_a values obtained were $pK_1 = 3.9$ and $pK_2 = 8.3$. The dissociation constants represent the protonated carbonyl oxygen (pK_1) and the hydroxamate hydroxyl proton (pK_2). The pK_2 value for **1** may be compared with the pK_a values for some organic hydroxamic acids, which are listed in Table I.[33] This comparison shows that the acidity of **1** is within the range expected for organic hydroxamic acids.

The formation constants of **1** with cobalt(II), nickel(II), copper(II), zinc(II), and iron(III) are given in Table II. These values are the average of at least four separate determinations. Activity coefficients were taken into account. The data summarized in Table II follow the general order of complex stabilities known as the Irving–Williams order,[34] which is Co(II) < Ni(II) < Cu(II) < Zn(II). This order says nothing about the relative stability of zinc compared to that of the cobalt or nickel complexes. Mellor and Malley[35] have given a more explicit order of stabilities: Zn(II) < Co(II) < Ni(II) < Cu(II), where the relationship between zinc, cobalt, and nickel is established. Inspection of Table II reflects the general agreement of the log K_1K_2 data with the Mellor–Malley order of stabilities.

Summary

The data obtained in this study support the proposed formulation for the first boron analogue of a hydroxamic acid as $(CH_3)_3N\cdot BH_2C(O)NHOH\cdot HCl$ (**1**). The compound may be represented by two resonance forms, $(CH_3)_3N\cdot BH_2C(=O^+H)\text{-}NHOH\cdot Cl^-$ and $(CH_3)_3N\cdot BH_2C(OH)=N^+HOH\cdot Cl^-$. The boranecarbohydroxamic acid complexes with transition-metal ions (Fe(III), Cr(III), Co(II), Ni(II), Zn(II)) give observed log K_1K_2 data in accordance with the Mellor–Malley order of stabilities.

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Registry No. **1**, 111496-18-5; **1**-d_3, 111496-19-6; $NH_2OH\cdot HCl$, 5470-11-1; $(CH_3)_3N\cdot BH_2$, 60788-33-2; $(CH_3)_3N\cdot BH_2C(O)NHOH\cdot HB(C_6H_5)_4$, 111496-20-9; $Cr[(CH_3)_3N\cdot BH_2C(O)NHO]_3$, 111496-22-1; $Fe[(CH_3)_3N\cdot BH_2C(O)NHO]_3$, 111496-21-0.

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Kinetics of Acid-Promoted Dissociation of Diamine–Diimine Macrocycle Complex Cations with Nickel(II) and Copper(II)

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The kinetics of the slow acid-promoted dissociation reactions of complex cations of nickel(II) and copper(II) with six diimine–diamine macrocycles, with 14, 15, and 16 ring members, have been studied in HCl–NaCl solutions (I = 2 mol L^{-1}) at 25 °C. The reaction rate for (5,5,7,13,15,15-hexamethyl-1,4,8,12-tetraazacyclopentadeca-7,12-diene)nickel(II) shows a linear dependence on $[H^+]$, with $k_{obsd} = 1.7\ (2) \times 10^{-5}[H^+]\ s^{-1}$. For several cations the first-order rate constants show a nonlinear dependence on $[H^+]$ with $k_{obsd} = A[H^+]/(1 + B[H^+])\ s^{-1}$, with the following parameters (A/L mol^{-1} s^{-1} and B/L mol^{-1}): (2,4,4,10,12,12-hexamethyl-1,5,9,13-tetraazacyclohexadeca-1,9-diene)copper(II), 9.0 (2) × 10^{-3}, 1.0 (2) (I = 1 mol L^{-1}); (5,7,7,13,15,15-hexamethyl-1,4,8,12-tetraazacyclopentadeca-4,12-diene)nickel(II), 1.4 (2) × 10^{-5}, 0.4 (1) (and 1.2 (2) × 10^{-4}, 0.17 (5) at 50 °C); (3,5,7,7,13,13,15-heptamethyl-1,4,8,12-tetraazacyclopentadeca-4,12-diene)nickel(II), 5.0 (5) × 10^{-7}, 0.13 (5). An "activated intermediate in equilibrium with starting material" mechanism is proposed for these reactions. A "protonation preequilibrium" mechanism is excluded by the absence of any spectroscopically detectable protonated tridentate macrocycle species. The reactions of other copper(II) cations show second-order dependence on $[H^+]$, with the following rate constants (L^2 mol^{-2} s^{-1}): (5,7,7,13,15,15-hexamethyl-1,4,8,12-tetraazacyclopentadeca-7,12-diene)copper(II), 8.7 (2) × 10^{-4} (I = 1 mol L^{-1}); (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)copper(II), 1.3 (2) × 10^{-7} (and 2.2 (2) × 10^{-6} at 50 °C); (5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene)copper(II), 1.5 (2) × 10^{-6} (and 2.1 (2) × 10^{-5} at 50 °C).

Introduction

A feature of the chemistry of complex cations of nickel(II) and copper(II) with aza macrocyclic ligands, which has been commented on from the beginnings of studies in this area, is the extreme resistance shown by many to acid hydrolysis.[1] Relatively few detailed kinetic studies of acid-promoted dissociation reactions of these complex cations have been reported,[2] but they can usually be accommodated within the same general mechanistic schemes as for complexes of noncyclic polyamines with these metal ions, although reaction rates may be slower by many orders of magnitude.[3]

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