teractions. Therefore, it should be expected to exhibit stronger antiferromagnetic interactions mainly of intermolecular nature. Actually, this is the case of the dimer $[Cu_2(\mu\text{-TPHA})(bpy)_2(H_2O)_2](ClO_4)_2$, prepared by us,[7] which indeed showed stronger magnetic interaction ($J \simeq -26$ cm^{-1}). Finally, it is worth noting that the magnetic exchange interactions, if any, of the μ-terephthalato dimers that do not possess suitable orbital pathways must be mainly intermolecular. However, it seems clear that the terephthalato dianion, under certain conditions, is an appropriate bridging unit to design magnetic systems with expected magnetic properties.

Registry No. **1**, 103817-49-8; **2**, 103817-51-2; **3**, 103834-81-7; **4**, 103817-53-4; **5**, 103817-55-6.

Supplementary Material Available: Table I (analytical data), Table II (extended Hückel parameters), Tables IV–VIII (variable-temperature magnetic susceptibility data), and Figures 2 and 4 (temperature dependence of $\chi_M T$ and $1/\chi_M$ for **2** and **4**) (15 pages). Ordering information is given on any current masthead page.

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Metal Complexes Containing the Trimethylamine–Carboxylatoborane Ligand: Synthesis and Characterization of $[M_3O((CH_3)_3N\cdot BH_2CO_2)_6R_3]^+X^-$ (M = Cr(III), Fe(III); R = H_2O, CH_3OH; X^- = NO_3^-, Cl^-)

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The coordination chemistry of Cr(III) and Fe(III) with the trimethylamine–carboxylatoborane ligand $[(CH_3)_3N\cdot BH_2CO_2^-]$ has been studied by using magnetic moments and infrared, proton and boron-11 NMR, and visible spectroscopies. The complexes have the formulation $[M_3O((CH_3)_3N\cdot BH_2CO_2)_6(R)_3]^+X^-$ (M = Cr(III), Fe(III); R = H_2O, CH_3OH; X^- = NO_3^-, Cl^-). The proposed structure contains three metal ions lying at the apices of an equilateral triangle, each coordinated to an oxygen atom located at the center of the triangle and each bridged by two acetate ligands. The carboxylatoborane ligand behaves similarly to carbon carboxylato ligands.

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*-ethylamide derivative, $(CH_3)_3N\cdot BH_2C(O)NHC_2H_5$, have demonstrated significant biological activity, with $(CH_3)_3N\cdot BH_2COOH$ showing 82% inhibition of tumor growth in the Ehrlich Ascites screen[2] and lowering serum cholesterol levels by 49% at low dosages.[3] The copper(II) complex of $(CH_3)_3N\cdot BH_2COOH$ shows increased biological activity compared to that of the free acid.[4] In addition to these biological studies, a study[5] of the basicity of $(CH_3)_3N\cdot BH_2COOH$ showed that replacement of the methylene group in betaine by the negatively charged BH_2 group increases the basicity of the carboxylate moiety by about 6 log units; e.g., the pK_a value for $(CH_3)_3NCH_2COOH$ is 1.83, whereas the corresponding value for $(CH_3)_3N\cdot BH_2COOH$ is 8.38. The latter observations coupled with questions arising during the study in our laboratory of the coordination chemistry of a boron analogue of a hydroxamic acid, $(CH_3)_3N\cdot BH_2C(O)NHOH\cdot HCl$,[6] necessitated a thorough study of the coordination chemistry of $(CH_3)_3N\cdot BH_2COOH$. Although Scheller et al. have reported[5] some stability constants of various boron analogues of glycine and *N*-methylated glycines $[(CH_3)_xNH_{3-x}\cdot BH_2COOH$ (x = 0–3)] with Zn(II) in solution, these complexes were not isolated. To date, only one example of an isolated coordination complex of $(CH_3)_3N\cdot BH_2COOH$ with a metal ion (Cu^{2+}) has been reported.[4] We here report the synthesis and characterization of Cr(III) and Fe(III) complexes of $(CH_3)_3N\cdot BH_2COOH$, both of which contain the cation $[M_3O((CH_3)_3N\cdot BH_2CO_2)_6R_3]^+$.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer. Solid samples were prepared as KBr disks. Proton and boron-11 NMR spectra were obtained on a JEOL FX90Q spectrometer. Standards were Me_4Si, DSS (^1H), and $Et_2O\cdot BF_3$ (^{11}B). Visible spectra were recorded on a Beckman Model 35 spectrophotometer with the concentration of the solutions being 1×10^{-2} M unless otherwise indicated. Room-temperature magnetic moments were determined by the relative Guoy method.[7] The Guoy calibrant was mercury(II) tetrakis(thiocyanato)cobaltate(II). All calculations, including diamagnetic corrections, were done according to standard procedure.[8] The following compounds were purchased and used without further purification: $(CH_3)_3N\cdot HCl$ (Aldrich), $NaBH_3CN$ (Aldrich), $Cr(NO_3)_3\cdot 9H_2O$ (J. T. Baker), $Fe(NO_3)_3\cdot 9H_2O$ (J. T. Baker), $FeCl_3\cdot 6H_2O$ (J. T. Baker). $(CH_3)_3N\cdot BH_2COOH$ was prepared[2] from the reaction of $(CH_3)_3N\cdot BH_2CN$[9] and $(C_2H_5)_3OBF_4$[10] followed by hydrolysis. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. Metal analyses for Fe(III) and Cr(III) were performed in our laboratory according to standard procedures.[11] Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ, or by Dr. David Holah, Lakehead University, Thunder Bay, Ontario, Canada.

Preparation of $(CH_3)_3N\cdot BH_2CO_2^-Na^+\cdot 0.25CH_3OH$ (1). A solution of Na_2CO_3 (0.53 g, 5.0 mmol) in water (10 mL) was added to a stirred solution of $(CH_3)_3N\cdot BH_2COOH$ (0.58, 5.0 mmol) in warm water (25 mL). The resulting mixture was kept at 35 °C for 0.5 h. The solvent was then removed by rotary evaporation to give a white solid, **1**, and the impurity $NaHCO_3$. The crude product was dissolved in methanol (15 mL), the insoluble $NaHCO_3$ (IR) filtered off, and the solvent removed under reduced pressure. An analytical sample was prepared by recrys-

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tallization from cold methanol (0.66 g, 90%): mp >260 °C; IR 2360 (BH), 1625 (antisym COO), 1450 (sym COO) cm^{-1}; ^{1}H NMR (D_2O): δ 2.65 (s, 9 H, $(CH_3)_3N$), 3.33 (s, 1 H, CH_3O); ^{11}B NMR (D_2O) δ −8.75 (t, BH_2, J_{B-H} = 92.7 Hz). Anal. Calcd for $C_4H_{11}BNO_2Na{\cdot}0.25CH_3OH$: C, 34.73; H, 8.23; N, 9.56. Found: C, 34.43; H, 8.56; N, 9.76. The product is soluble in water and alcohols but insoluble in organic solvents.

Preparation of $[Fe_3O((CH_3)_3N{\cdot}BH_2CO_2)_6(CH_3OH)_3]NO_3{\cdot}CH_3CN$ (2). A solution of **1** (0.53 g, 3.6 mmol) in methanol (15 mL) was added to a stirred solution of $Fe(NO_3)_3{\cdot}9H_2O$ (0.44 g, 1.1 mmol) in methanol (10 mL). The color of the Fe(III) solution changed from orange to dark red immediately upon addition of the solution containing the ligand. After the mixture was stirred for 0.5 h, the solvent was removed by rotary evaporation to give a dark red solid along with $NaNO_3$ as an impurity. The crude complex was dissolved in CH_3CN (25 mL), the insoluble $NaNO_3$ (IR) filtered off, and the solvent removed under reduced pressure. An analytical sample was prepared by recrystallization from CH_3CN/pentane (0.34 g, 86%): mp 140–142 °C dec; IR 3400 (OH), 2380 (BH), 1668 (antisym COO), 1485 (sym COO), 1380 (antisym ONO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.75 (br s, 57 H, $(CH_3)_3N$, CH_3CN), 3.71 (br s, 9 H, CH_3O); ^{11}B NMR (CD_3COCD_3) δ −12.0 (t, BH_2, J_{B-H} = 103 Hz). Anal. Calcd for $C_{27}H_{78}B_6N_7O_{19}Fe_3{\cdot}CH_3CN$: C, 32.29; H, 7.57; N, 10.39; Fe, 15.54. Found: C, 31.77; H, 7.48; N, 10.33; Fe, 15.67. The complex is soluble and stable in acetonitrile, acetone, chloroform, alcohol, and methylene chloride. It decomposes slowly in aqueous solution, as evidenced by the formation of a brown precipitate that does not exhibit infrared absorptions characteristic of B–H.

Preparation of $[Fe_3O((CH_3)_3N{\cdot}BH_2CO_2)_6(CH_3OH)_3]Cl$ (3). A solution of **1** (0.65 g, 4.4 mmol) in methanol (20 mL) was added to a stirred solution of $FeCl_3{\cdot}6H_2O$ (0.39, 1.4 mmol) in methanol (10 mL). The color of the Fe(III) solution changed from orange to dark red immediately upon addition of the solution containing the ligand. After the mixture was stirred for 0.5 h, the solvent was removed by rotary evaporation to give a dark red solid and NaCl as an impurity. The crude complex was dissolved in CH_2Cl_2 (30 mL), the insoluble NaCl (standard chloride test) filtered off, and the solvent removed under reduced pressure. An analytical sample was prepared by recrystallization from CH_2Cl_2/diethyl ether (0.44 g, 93%): mp 62–64 °C dec; IR 3400 (OH), 2950 (CH), 2380 (BH), 1668 (antisym COO), 1485 (sym COO) cm^{-1}; ^{1}H NMR (CD_3CN) δ 2.71 (br s, 54 H, $(CH_3)_3N$), 3.41 (br s, 9 H, CH_3O); ^{11}B NMR (CD_3CN) δ −15.5 (t, BH_2, J_{B-H} = 103 Hz). Anal. Calcd for $C_{27}H_{78}B_6N_6O_{16}Fe_3Cl$: C, 32.01; H, 7.78; N, 8.32; Fe, 16.58. Found: C, 31.82; H, 7.38; N, 8.31; Fe, 16.45. The complex is soluble in acetone, acetonitrile, chloroform, methylene chloride, and alcohol. It decomposes slowly in water, as evidenced by the formation of a brown precipitate that does not exhibit infrared absorptions characteristic of B–H. The complex gives a positive test for chloride ion when a solution of $AgNO_3$ is added, but the presence of the B–H hydrogens makes quantitative analysis difficult since silver deposits on the sides of the container.

Preparation of $[Cr_3O((CH_3)_3N{\cdot}BH_2CO_2)_6(H_2O)_3]NO_3{\cdot}CH_3OH{\cdot}CH_3CN$ (4). A solution of **1** (1.1 g, 7.6 mmol) in methanol (15 mL) was added to a stirred solution of $Cr(NO_3)_3{\cdot}9H_2O$ (1.0 g, 2.5 mmol) in methanol (15 mL). The color of the Cr(III) solution changed from aquamarine to light green immediately upon addition of the solution containing the ligand. After the mixture was stirred for 0.5 h, the solvent was removed by rotary evaporation to give a dark green solid and $NaNO_3$ as an impurity. The crude complex was dissolved in CH_3CN (20 mL), the insoluble $NaNO_3$ (IR) filtered off, and the solvent removed under reduced pressure. An analytical sample was prepared by recrystallization from CH_3CN/diethyl ether (0.81 g, 92%): mp 112–113 °C dec; IR 3440 (OH), 2950 (CH), 2385 (BH), 1670 (antisym COO), 1485 (sym COO), 1380 (antisym ONO_2) cm^{-1}; ^{1}H NMR (CD_3CN) δ 2.72 (br s, 57 H, $(CH_3)_3N$, CH_3CN), 3.37 (br s, 3 H, CH_3O); ^{11}B NMR (CH_3CN) δ −11.0 (t, BH_2, J_{B-H} = 100 Hz). Anal. Calcd for $C_{24}H_{72}B_6N_7O_{19}Cr_3{\cdot}CH_3OH{\cdot}CH_3CN$: C, 30.62; H, 7.54; N, 10.61; Cr, 14.76. Found: C, 29.92; H, 7.44; N, 10.91; Cr, 14.92. The complex is soluble and stable in acetone, acetonitrile, alcohol, and water.

Results and Discussion

The Trimethylamine–Carboxylatoborane Ligand $(CH_3)_3N{\cdot}BH_2COO^-$ (1′). The infrared absorption bands of the trimethylamine–carboxylatoborane sodium salt (**1**) assigned to the anion (**1′**) differ markedly from that of the free acid $(CH_3)_3N{\cdot}BH_2COOH$ (Table I). The strong and broad absorption band at 3130 cm^{-1} in $(CH_3)_3N{\cdot}BH_2COOH$, assigned to the O–H stretching vibration,[12] is not observed in the spectrum of **1′**. Also, the spectrum of $(CH_3)_3N{\cdot}BH_2COOH$ shows that a strong absorption occurs at 1650 cm^{-1}, which is assigned to the carbonyl (C=O) stretching vibration.[12] However, in the spectrum of **1′** this band disappears and two new bands appear at 1625 and 1450 cm^{-1}, which may be assigned to the antisymmetric and symmetric stretching vibrations of the carbon–oxygen (COO) bonds.[13] Finally, the in-plane and out-of-plane OH deformation absorptions at 1375 and 915 cm^{-1}, respectively, in the spectrum of $(CH_3)_3N{\cdot}BH_2COOH$ have disappeared in the spectrum of **1′**, as expected due to abstraction of the carboxyl O–H proton in $(CH_3)_3N{\cdot}BH_2COOH$ by Na_2CO_3.

Table I. Infrared Spectral Results and Assignments for Trimethylamine–Carboxyborane and the Trimethylamine–Carboxylatoborane Ion[a]

$(CH_3)_3N{\cdot}BH_2COOH$	$(CH_3)_3N{\cdot}BH_2CO_2^-Na^+{\cdot}0.25CH_3OH$ (1)	assignmt
3130 m, br[b]		ν(OH)
1650 s, sh[b]		ν(C=O)
	1625 s, sh[c]	$\nu_{antisym}$(COO)
	1450 s, sh[c]	ν_{sym}(COO)
3175 s, sh[c]		$\nu_{in\text{-}plane}$(OH def)
915 m, br[c]		$\nu_{out\text{-}of\text{-}plane}$(OH def)
650 m, sh[c]		ν(OCO) skeletal

[a] All results in cm^{-1}. Abbreviations: br, broad; s, strong;, m, medium; sh, sharp. [b] Reference 12. [c] This work.

Further assignment of the infrared absorptions associated with the carboxylate group in $(CH_3)_3N{\cdot}BH_2COOH$ was accomplished by a deuteration study. The acid, $(CH_3)_3N{\cdot}BH_2COOH$, was stirred in D_2O for 2 h and the deuterated compound isolated. Comparing the changes observed upon deuteration with the changes observed when acetic acid is deuterated[14] allows the assignment of the out-of-plane OH deformation, the in-plane OH deformation, and the OCO skeletal deformation of $(CH_3)_3N{\cdot}BH_2COOH$ (Table I). This study represents the first systematic assignment of these bands for trimethylamine–carboxyborane. Previously, only the carbonyl (C=O) and carboxyl O—H stretching vibrations had been assigned.[12] We also note that the absorption band at 2375 cm^{-1} in the spectrum of $(CH_3)_3N{\cdot}BH_2COOH$, assigned to the B–H stretching vibration, does not disappear in the spectrum of the deuterated analogue, indicating that the B–H bond remains intact under the deuteration conditions used.

Metal Complexes. The reaction of 3 equiv of **1** with 1 equiv of iron(III) nitrate, iron(III) chloride, or chromium(III) nitrate in methanol results in each case in the formation of a complex. This conclusion is supported in part by the fact that the colors of the solutions containing the metal ion change immediately upon addition of the solution containing **1**. The ^{11}B NMR spectra of these solutions show a 1:2:1 triplet, indicating that the BH_2^- moiety in the trimethylamine–carboxylatoborane ligand remains intact. No other boron-containing species were observed. There was no bubbling noted in the solution when the metal and **1** were mixed. These results support the conclusion that decomposition of **1** did not occur during the observed color change of the solution when reactants were mixed.

The trinuclear basic acetates of Cr(III) and Fe(III) were first prepared by Weinland.[15] Their magnetic behavior was investigated by Welo[16] and successfully interpreted by Kambe.[17] The structures of these complexes were correctly predicted by Orgel.[18] Subsequent X-ray diffraction studies[19] have firmly established the trinuclear nature of the complex $[Cr_3O(CH_3CO_2)_6(H_2O)_3]$-

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Table II. Ligand Field Bands of $[Cr_3O((CH_3)_3N\cdot BH_2CO_2)_6R_3]^+$ and $[Cr_3O(CH_3CO_2)_6R_3]^+$ in Various Solvents[a]

	$[Cr_3O((CH_3)_3N\cdot BH_2CO_2)_6R_3]^+$		$[Cr_3O(CH_3CO_2)_6R_3]^{+\,23}$	
terminal ligand R	band I, nm[a] ($^4A_{2g} \rightarrow {}^4T_{2g}$)	band II, nm[a] ($^4A_{2g} \rightarrow {}^4T_{1g}$)	band I, nm ($^4A_{2g} \rightarrow {}^4T_{2g}$)	band II, nm ($^4A_{2g} \rightarrow {}^4T_{1g}$)
DMA	602 (55)	455 (55)	602	453
Me_2SO	595 (47)	450 (44)	597	453
OH^-	592 (37)	445 (33)	594	448
H_2O	583 (33)	434 (27)	579	437
MeOH	586 (39)	439 (34)	585	441
EtOH	588 (38)	440 (33)	589	443
py	571 (34)	431 (30)	568	433

[a] Molar extinction coefficients (per monomer) are given in parentheses: DMA, dimethylacetamide; Me_2SO, dimethyl sulfoxide; py, pyridine.

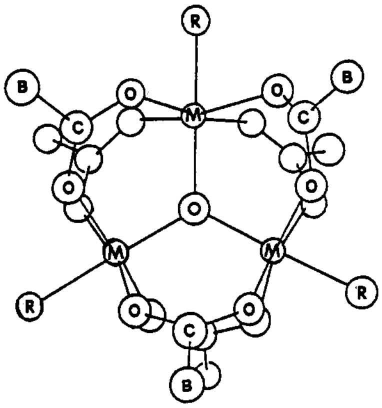

Figure 1. Proposed framework structure of $[M_3O((CH_3)_3N\cdot BH_2CO_2)_6R_3]^+$ (M = Cr(III), Fe(III); R = MeOH, H_2O).

$Cl\cdot 2H_2O$. The three chromium(III) ions, each pair bridged by two acetate ligands, lie at the apices of an equilateral triangle. The trigonally coordinated oxygen atom in the center of the triangle and the three terminal ligands complete the octahedral coordination at each chromium(III) ion. The analogous trinuclear iron(III) acetate is isostructural.[19] The synthetic method and resulting characterization utilized for the synthesis of our trinuclear metal carboxylatoborane complexes (**2**–**4**) is similar to that utilized for the synthesis of the analogous trinuclear metal acetato complexes.[20–22] Comparison of the latter studies to our data supports the conclusion that the reaction of 3 equiv of **1** with 1 equiv of iron(III) or chromium(III) yields compounds of analogous structure, i.e., the unipositive trinuclear metal carboxylatoborane complexes $[Fe_3O((CH_3)_3N\cdot BH_2CO_2)_6(CH_3OH)_3]^+$ (**2**, **3**) and $[Cr_3O((CH_3)_3N\cdot BH_2CO_2)_6(H_2O)_3]^+$ (**4**). Supporting data for the proposed structure (Figure 1) will be given by comparing the infrared and visible spectroscopic data and the magnetic moment data for the trimethylamine–carboxylatoborane complexes with the data available for the corresponding acetato complexes.

Visible Spectra. The visible spectrum of the chromium complex, **4**, in methanol is shown in Figure 2. The spectrum is characterized by a pronounced shoulder at 680 nm of the first spin-allowed band, a weak absorption at 730 nm, and a set of four weak bands in the near-ultraviolet region. The terminally coordinated water molecules in $[Cr_3O((CH_3)_3N\cdot BH_2CO_2)_6(H_2O)_3]^+$ and $[Cr_3O(CH_3CO_2)_6(H_2O)_3]^{+\,23}$ are labile and may be replaced by a number of ligands of varying donor strength (Table II). The complexes give analogous results. The large Cr–Cr separation[24] in the trinuclear chromium(III) acetato complex (3.28 Å) precludes any significant metal–metal bonding, and for this reason the visible absorption bands are characteristic of 3d–3d transitions localized at the metal ions. On this basis, the first absorption band in the visible spectrum of $[Cr_3O((CH_3)_3N\cdot BH_2CO_2)_6(H_2O)_3]^+$ (**4**) may be assigned the electronic transition $^4A_{2g} \rightarrow {}^4T_{2g}$, while the second band, centered around 430–450 nm, may be assigned to the transition $^4A_{2g} \rightarrow {}^4T_{1g}$.

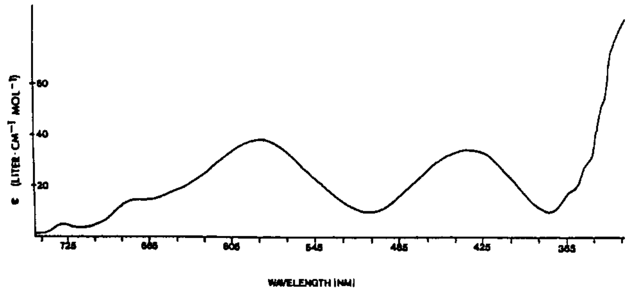

Figure 2. Visible spectrum of $[Cr_3O((CH_3)_3N\cdot BH_2CO)_6(H_2O)_3]NO_3\cdot CH_3OH\cdot CH_3CN$ (**4**) in methanol at 25 °C.

Table III. Infrared Spectral Results for Carboxylato Complexes

compd	$\nu_{antisym}$-(COO)[a]	ν_{sym}-(COO)[a]	Δ[b]
$CH_3CO_2^-Na^+$	1578	1414	164
$(CH_3)_3N\cdot BH_2CO_2^-Na^+\cdot 0.25CH_3OH$ (**1**)	1625	1450	175
$[Fe_3O(CH_3CO_2)_6(H_2O)_3]Cl\cdot 5H_2O$	1595	1450	145
$[Fe_3O((CH_3)_3N\cdot BH_2CO_2)_6(CH_3OH)_3]$-$NO_3\cdot CH_3CN$ (**2**)	1668	1485	183
$[Fe_3O((CH_3)_3N\cdot BH_2CO_2)_6(CH_3OH)_3]$-Cl (**3**)	1668	1485	183
$[Cr_3O((CH_3)_3N\cdot BH_2CO_2)_6(H_2O)_3]N$-$O_3\cdot CH_3OH\cdot CH_3CN$ (**4**)	1670	1485	185

[a] All results in cm^{-1}. [b] $\Delta = \nu_{antisym}(COO) - \nu_{sym}(COO)$.

The positions of the two absorption bands in the visible spectrum of **4** are directly comparable to those found for the acetate analogue, $[Cr_3O(CH_3CO_2)_6(H_2O)_3]Cl\cdot 2H_2O$. This result appears to be inconsistent with the fact that the trimethylamine–carboxylatoborane ligand, **1′**, is a stronger base than the acetato ligand, and consequently, one might expect some difference in the position of the absorption bands found for each complex. However, the additional electron density donated to the metal atom from the carboxylatoborane ligand is probably such a small overall perturbation to the system that the change in energy of the d orbitals is sufficiently small so that it is not detectable in the broad absorption bands. Unfortunately, support for this cannot be obtained by comparison to trinuclear chromium(III) acetato complexes because spectral data are not reported regarding the effect changing the basicity of the acetato ligands has on the position of the absorption bands.

The visible spectra of the trinuclear iron(III) trimethylamine–carboxylatoborane complexes (**2**, **3**) in methanol are very broad and poorly resolved; consequently, no specific bands could be assigned. It has been noted that little is known of the details of iron(III) spectra in general, because of the tendency of the trivalent ion to have charge-transfer bands in the near-ultraviolet

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Table IV. Magnetic Susceptibilities[a] and Magnetic Moments of Metal Complexes of Trimethylamine–Carboxylatoborane

compd	specific suscept × 10^6	molar suscept × 10^3	cor[b] molar suscept × 10^3	μ_{eff}, μ_B
$[Cr_3O((CH_3)_3N{\cdot}BH_2CO_2)_6(H_2O)_3]NO_3{\cdot}CH_3OH{\cdot}CH_3CN$ (**4**)	4.507[c]	4.762	5.335	3.57
$[Fe_3O((CH_3)_3N{\cdot}BH_2CO_2)_6(CH_3OH)_3]NO_3{\cdot}CH_3CN$ (**2**)	3.740[d]	4.033	4.609	3.32
$[Fe_3O((CH_3)_3N{\cdot}BH_2CO_2)_6(CH_3OH)_3]Cl$ (**3**)	3.949[d]	3.991	4.541	3.29

[a] All in units of $cm^3{\cdot}g^{-1}$. [b] Corrected for the diamagnetism of the ligand. [c] Specific susceptibility per Cr atom. [d] Specific susceptibility per Fe atom.

region with strong low-energy wings in the visible region that obscure the very weak, spin-forbidden d–d bands.[25]

Infrared Spectra. Infrared studies are useful in assigning the bonding in the trinuclear metal carboxylatoborane complexes $[M_3O((CH_3)_3N{\cdot}BH_2CO_2)_6R_3]^+$ (M = Fe(III), R = CH_3OH (**2**, **3**); M = Cr(III), R = H_2O (**4**)). The infrared spectrum of **3** consists of absorption bands characteristic of O–H, C–H, B–H, antisymmetric COO, and symmetric COO stretching vibrations. The strong absorption at 1668 cm^{-1}, the antisymmetric COO stretching vibration, and the strong band at 1485 cm^{-1}, the symmetric COO stretching vibration, give a Δ value of 183 cm^{-1}, only slightly different from the ionic value of 175 cm^{-1} ($\Delta = \nu_{\text{antisym}}(\text{COO}) - \nu_{\text{sym}}(\text{COO})$). Both absorptions occur at higher frequency than those of the free ligand. These data are consistent with the assignment of a bidentate bridging coordination mode for the trimethylamine–carboxylatoborane ligand in **3** since (1) it has been suggested[26,27] that bidentate bridging coordination should give Δ values similar to ionic values, (2) analogous results are obtained from the IR data[4b,c] for $[Cu((CH_3)_3N{\cdot}BH_2CO_2)_2{\cdot}(CH_3)_3N{\cdot}BH_2COOH]_2$, which exhibits (X-ray structure)[4d] bidentate bridging coordination for **1′**, and (3) analogous results are also obtained from the infrared spectra of known acetate complexes that exhibit bidentate bridging coordination.[24] (For example, $[Fe_3O(CH_3CO_2)_6(H_2O)_3]Cl{\cdot}5H_2O$ (Table III) contains a bidentate bridging acetato ligand, it has a Δ value similar to that for the free ionic acetate, and both the antisymmetric and symmetric carboxyl frequencies increase from the free ligand value.)

The infrared spectrum of **2** is essentially identical with that of **3**, except for a strong absorption at 1380 cm^{-1} and a sharp, weak band at 2210 cm^{-1}. The former band may be assigned to the $O–NO_2$ antisymmetric stretching frequency of the nitrate ion.[28] The latter is assigned to the C≡N stretching vibration in the acetonitrile solvent molecule. Thus, on the basis of the values of Δ and the antisymmetric and symmetric COO stretching frequencies (Table III), **1′** is assigned a bidentate bridging coordination mode in both the trinuclear iron(III) complexes (**2**, **3**).

Finally, the infrared spectrum of **4** shows absorptions characteristic of O–H, C–H, B–H, C–N, antisymmetric COO, symmetric COO, and antisymmetric $O–NO_2$ stretching vibrations. The Δ value (185 cm^{-1}) and the increase in antisymmetric and symmetric stretching frequencies are consistent with a bidentate bridging coordination mode for **1′** in this complex also.

Magnetic Susceptibilities. The specific, molar, and corrected molar susceptibilities and the magnetic moments (μ_{eff}) of the trimethylamine–carboxylatoborane complexes (**2**–**4**) are listed in Table IV. The magnetic moments of $[Fe_3O((CH_3)_3N{\cdot}BH_2CO_2)_6(CH_3OH)_3]NO_3{\cdot}CH_3CN$ (**2**) and $[Fe_3O((CH_3)_3N{\cdot}BH_2CO_2)_6(CH_3OH)_3]Cl$ (**3**) are 3.32 and 3.29 μ_B, respectively. These results reveal that the room-temperature magnetic moments are significantly reduced from the value expected for high-spin iron(III), which is normally about 5.92 μ_B. In addition, the magnetic moment of $[Cr_3O((CH_3)_3N{\cdot}BH_2CO_2)_6(H_2O)_3]NO_3{\cdot}CH_3CN{\cdot}CH_3OH$ (**4**) is 3.57 μ_B, still below the spin-only value expected of approximately 3.9 μ_B. These room-temperature magnetic moment data further support that the complexes **2**–**4** possess the trinuclear M_3O unit since they are in the same range observed for the room-temperature magnetic moment data obtained for the analogous trinuclear metal acetato complexes of iron(III) and chromium(III).[16,17] For example, $[Fe_3O(CH_3CO_2)_6(H_2O)_3]Cl{\cdot}2H_2O$ has a room-temperature magnetic moment of 3.23 μ_B.

Summary

The data obtained in this study unequivocally support the proposed structure (Figure 1) for these complexes, showing that the carboxylatoborane ligand can behave similarly to the acetato ligand, acting as a bidentate bridging ligand. The biological activity of these complexes as well as other coordination modes of the carboxylatoborane ligand will be reported in a later publication.

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Registry No. **1**, 103904-11-6; **2**, 103904-13-8; **3**, 103904-14-9; **4**, 103904-16-1; $(CH_3)_3N{\cdot}BH_2COOH$, 60788-33-2; $[Cr_3O((CH_3)_3N{\cdot}BH_2CO_2)_6R_3]^+$ (R = DMA), 103904-17-2; $[Cr_3O((CH_3)_3N{\cdot}BH_2CO_2)_6R_3]^+$ (R = Me_2SO), 103904-18-3; $[Cr_3O((CH_3)_3N{\cdot}BH_2CO_2)_6R_3]^{2-}$ (R = OH^-), 103904-19-4; $[Cr_3O((CH_3)_3N{\cdot}BH_2CO_2)_6R_3]^+$ (R = MeOH), 103904-20-7; $[Cr_3O((CH_3)_3N{\cdot}BH_2CO_2)_6R_3]^+$ (R = EtOH), 103904-21-8; $[Cr_3O((CH_3)_3N{\cdot}BH_2CO_2)_6R_3]^+$ (R = py), 103904-22-9; $[Cr_3O(CH_3CO_2)_6R_3]^+$ (R = DMA), 103904-23-0; $[Cr_3O(CH_3CO_2)_6R_3]^+$ (R = Me_2SO), 103904-24-1; $[Cr_3O(CH_3CO_2)_6R_3]^{2-}$ (R = OH^-), 103904-25-2; $[Cr_3O(CH_3CO_2)_6R_3]^+$ (R = H_2O), 36502-05-3; $[Cr_3O(CH_3CO_2)_6R_3]^+$ (R = MeOH), 103904-26-3; $[Cr_3O(CH_3CO_2)_6R_3]^+$ (R = EtOH), 103932-97-4; $[Cr_3O(CH_3CO_2)_6R_3]^+$ (R = py), 103904-27-4.

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