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Synthesis and Characterization of Cobalt(III), Cobalt(II), Zinc(II), and Calcium(II) Complexes Containing the Trimethylamine–Boranecarboxylato Ligand $(CH_3)_3N{\cdot}BH_2COO^-$

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The coordination chemistry of Co(III), Co(II), Zn(II), and Ca(II) with the trimethylamine–boranecarboxylato ligand, obtained from $(CH_3)_3N{\cdot}BH_2CO_2^-Na^+{\cdot}0.25CH_3OH$ (**1**), has been studied by using infrared, proton NMR, boron-11 NMR, and visible spectroscopies. The cobalt(III) complex, derived from *trans*-$[Co(en)_2Cl_2]Cl$, contains the cation *cis*-$[Co(en)_2((CH_3)_3N{\cdot}BH_2CO_2)_2]^+$, where the coordination mode of the trimethylamine–boranecarboxylato ligand is monodentate. The cobalt(II), zinc(II), and calcium(II) complexes derived from the respective metal nitrates consist of the cation $[M((CH_3)_3N{\cdot}BH_2CO_2)]^+$, where the ligand functions as a bidentate chelating ligand.

Introduction

There has been a great deal of interest recently in the synthesis and characterization of a series of isoelectronic and isosteric boron analogues of α-amino acids. Spielvogel et al. have prepared the boron analogues of glycine[1] and N-methylated glycines[2,3], $(CH_3)_xNH_{3-x}{\cdot}BH_2COOH$ ($x = 0$–3), as well as their *N*-ethylcarbamoyl derivatives.[2,4] Replacement of the methylene group in glycine and N-methylated glycines by a negatively charged BH_2 group increases the basicity of the carboxylate group by about 6.6 log units.[5] Thus, although boron analogues of α-amino acids are similar in geometric structure to organic amino acids, they provide an important difference in electronic structure, which results in significant differences in chemical and biological behavior. Both trimethylamine–carboxyborane, $(CH_3)_3N{\cdot}BH_2COOH$, and its N-ethylcarbamoyl derivative, $(CH_3)_3N{\cdot}BH_2C(O)NHC_2H_5$, have demonstrated significant biological activity. For example, $(CH_3)_3N{\cdot}BH_2COOH$ afforded 82% inhibition of tumor growth in the Ehrlich Ascites screen[6] and lowered serum cholesterol levels by 49% at low dosages.[7] In the complex between $(CH_3)_3N{\cdot}BH_2COOH$ and copper(II), antitumor inhibition was increased to 98% compared to the free ligand value of 82%.[8a,b] This change in biological activity upon coordination suggested that a further examination of the complexation of the trimethylamine–boranecarboxylato ligand, $(CH_3)_3N{\cdot}BH_2CO_2^-$ (**1′**) to metal ions might prove fruitful if only because of the possibility of increasing the biological activity of the boron analogue. There were, however, other aspects of such a study that would also be extremely valuable. Changes in infrared and ^{11}B NMR spectra observed upon coordination of **1′** could provide potentially useful information for studies on the nature of the coordination chemistry of a boron analogue of a hydroxamic acid.[9a] This study could also show if insertion of the BH_2^- moiety affects the coordinating ability of the trimethylamine–boranecarboxylato ligand, $(CH_3)_3N{\cdot}BH_2CO_2^-$ (**1′**), in comparison to organic carboxylato ligands.

We have previously reported the synthesis and characterization of Cr(III) and Fe(III) complexes where **1′** acts as a bridging bidentate ligand.[9b] We have found that other coordination modes can be assumed by this ligand, and these are reported herein.

Experimental Section

Reagents and Solvents. All inorganic chemicals were analytical reagent grade and used without further purification. All organic solvents were dried by standard procedures[10] and stored over 4-Å molecular sieves under nitrogen.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer using samples prepared as KBr pellets. Proton NMR were recorded at 90 MHz on a JEOL-FX90Q instrument with Me_4Si or DDS as internal standard. Boron-11 NMR spectra were obtained at 32.1 MHz with chemical shifts relative to the external standard, $(C_2H_5)_2O{\cdot}BF_3$. Visible spectra were recorded on 10^{-2} M samples with a Beckman Model 35 spectrophotometer. Room-temperature magnetic moments were determined by the relative Gouy method[11] using the calibrant mercury(II) tetrakis(thiocyanato)cobaltate(II). All calculations, including diamagnetic corrections, were done according to standard procedure.[12] Melting points were determined on a Thomas Hoover capillary apparatus and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ 85018, or by Dr. David G. Holah, Lakehead University, Thunder Bay, Ontario, Canada P7B 5E1. Metal analyses were performed in our laboratory by using standard gravimetric and spectrophotometric techniques.[13]

Synthesis of the Compounds. Trimethylamine–Carboxyborane. The compound $(CH_3)_3N{\cdot}BH_2COOH$ was prepared according to the method of Spielvogel.[2]

***trans*-Dichlorobis(ethylenediamine)cobalt(III) Chloride.** The complex *trans*-$[Co(en)_2Cl_2]Cl$ was prepared as reported in the literature.[14]

$(CH_3)_3N{\cdot}BH_2CO_2^-Na^+{\cdot}0.25CH_3OH$ (1). The trimethylamine–boranecarboxylato sodium salt was prepared as reported earlier.[9b]

***cis*-$[Co(en)_2((CH_3)_3N{\cdot}BH_2CO_2)_2]Cl{\cdot}2.5H_2O{\cdot}0.5CH_3OH$ (2).** A solution of **1** (0.53 g, 3.6 mmol) in water (10 mL) was added to a stirred solution of *trans*-$[Co(en)_2Cl_2]Cl$ (0.50 g, 1.8 mmol) in water (15 mL). The color of the Co(III) solution immediately changed from green to purple upon addition of the solution containing **1′**. After the mixture was stirred for 0.5 h, the solvent was removed by rotary evaporation to give a crude product. The desired complex was dissolved in CH_3CN (35 mL), the insoluble NaCl (0.21 g, 3.6 mmol; standard chloride test) removed by filtration, and the solvent removed under reduced pressure to give an analytical sample (0.64 g, 70%): mp > 250 °C dec; IR (KBr disk) 3440 (OH), 3100 (NH), 2950 (CH), 2350 (BH), 1655 (antisym COO), 1450 (sym COO) cm^{-1}; ^1H NMR (D_2O) δ 2.60 (s, 8 H, CH_2), 2.67 (s, 18 H, $(CH_3)_3N$), 3.35 (br s, 2 H, CH_3O), 4.75 (s, 14 H, HOD); ^{11}B NMR (CD_3CN) δ −9.44 (t, BH_2, $J_{B-H} = 95.2$ Hz). Anal. Calcd for $C_{12}H_{38}B_2N_6O_4CoCl{\cdot}2.5H_2O{\cdot}0.5CH_3OH$: C, 29.58; H, 8.94; N, 16.56;

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Co. 11.61. Found: C, 29.56; H, 8.18; N, 16.48; Co, 11.54.

$Co((CH_3)_3N\cdot BH_2CO_2)NO_3\cdot CH_3CN\cdot 3CH_3OH$ (3). Trimethylamine–Boranecarboxylato Complexes 3–5. A solution containing 1 equiv of **1** was added to a stirred solution containing 1 equiv of the appropriate hydrated metal nitrate in alcohol. In the case of complex **3**, a color change from pink to purple immediately resulted; however, with complexes **4** and **5**, a suspension resulted when alcoholic solutions of **1** and the metal nitrate were mixed. After the mixture was stirred for 0.5 h, the solvent was removed by rotary evaporation to give a crude product. The desired complex was dissolved in an appropriate organic solvent (see data relevant to each compound). One equivalent of insoluble $NaNO_3$ (IR) was removed by filtration, and the solvent was removed under reduced pressure. Analytical results obtained from each complex are as follows. **$Co((CH_3)_3N\cdot BH_2CO_2)NO_3\cdot CH_3CN\cdot 3CH_3OH$ (3)** (CH_3CN, diethyl ether; 0.60 g, 89%): mp 118–120 °C dec; IR (KBr disk) 3500 (OH), 2940 (CH), 2378 (BH), 1616 (antisym COO), 1505 (antisym ONO_2), 1450 (sym COO) 1290 (sym ONO_2) cm^{-1}; ^1H NMR (CD_3COCD_3), δ 2.75 (br s, 12 H, $(CH_3)_3N$, CH_3CN), 3.38 (br s, 9 H, CH_3O); ^{11}B NMR (CD_3COCD_3) δ −11.0 (t, BH_2, $J_{B-H} = 103$ Hz). Anal. Calcd for $C_4H_{11}BN_2O_5Co\cdot CH_3CN\cdot 3CH_3OH$: C, 28.90; H, 7.01; N, 11.23; Co, 15.75. Found: C, 28.18; H, 6.75; N, 10.76; Co, 15.70. The complex is soluble in acetone, acetonitrile, alcohol, and water but is insoluble in ether and pentane. **$Ca((CH_3)_3N\cdot BH_2CO_2)NO_3\cdot CH_3COCH_3\cdot 0.5H_2O$ (4).** (acetone, pentane; 0.58 g, 92%): mp 159–161 °C dec; IR (KBr disk) 3450 (OH), 2940 (CH), 2380 (BH), 1710 (C=O), 1620 (antisym COO), 1450 (sym COO), 1380 (antisym ONO_2) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 2.05 (m, 6 H, CH_3COCH_3), 2.73 (s, 9 H, $(CH_3)_3N$); ^{11}B NMR (D_2O) δ −9.00 (t, BH_2, $J_{B-H} = 95.2$ Hz). Anal. Calcd for $C_4H_{11}BN_2O_5Ca\cdot CH_3COCH_3\cdot 0.5H_2O$: C, 29.49; H, 6.36; N, 9.83; Ca, 14.06. Found: C, 29.49; H, 6.59; N, 9.90; Ca, 14.00. **$Zn((CH_3)_3N\cdot BH_2CO_2)NO_3\cdot CH_3CH_2OH$ (5).** (ethanol, diethyl ether; 2.2 g, 87%): mp 235–237 °C dec; IR (KBr disk) 3450 (OH), 2940 (CH), 2380 (BH), 1480 (antisym COO), 1405 (sym COO), 1380 (antisym ONO_2) cm^{-1}; ^1H NMR (CD_3COCD_3), δ 1.02 (t, 3 H, CH_3), 2.64 (s, 9 H, $(CH_3)_3N$), 3.86 (q, 2 H, CH_2); ^{11}B NMR (CD_3COCD_3) δ −9.68 (t, BH_2, $J_{B-H} =$ 97.6 Hz). Anal. Calcd for $C_4H_{11}BN_2O_5Zn\cdot CH_3CH_2OH$: C, 24.90; H, 5.94; N, 9.68; Zn, 22.59. Found: C, 24.97; H, 6.09; N, 9.72; Zn, 22.47. The complex is soluble in acetone, acetonitrile, alcohol, and water but is insoluble in ether, pentane, and benzene.

Results and Discussion

Synthetic Methods. Cobalt(III). The synthetic method reported herein for the preparation of **2** is relatively straightforward. The reaction of 2 equiv of **1** with 1 equiv of *trans*-$[Co(en)_2Cl_2]Cl$ in water results in the formation of a complex, which is evidenced by the fact that the color of the cobalt(III) solution immediately changes from green to purple upon addition of the solution containing **1′**. The ^{11}B NMR spectrum of this solution shows only a 1:2:1 triplet at −9.4 ppm, due to the BH_2^- moiety, indicating that the ligand has not decomposed and that a new boron containing compound has formed.

A synthetic method reporting[15] the preparation of analogous (haloacetato)bis(ethylenediamine)cobalt(III) complexes of the general formula *cis*-$[Co(en)_2R_2]^+$ requires heating a solution of $[Co(en)_2CO_3]ClO_4$ and the haloacetic acid (R) in water for 3–4 h at 80 °C. This method was attempted for trimethylamine–carboxyborane but no reaction occurred since the $(CH_3)_3N\cdot BH_2COOH$ could be recovered from the reaction mixtures. This result may be rationalized by considering the first two steps in the mechanism of the reaction of $[Co(en)_2CO_3]^+$ with a carboxylic acid in water (eq 1 and 2).[15] The hydrogen carbonato complex

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+ \qquad (1)$$

$$[Co(en)_2CO_3]^+ + H_3O^+ \rightleftharpoons [Co(en)_2HCO_3]^{2+} + H_2O \qquad (2)$$

formed in eq 2 exchanges HCO_3^- with H_2O and the aquated product reacts with the carboxylato ion ($RCOO^-$) to form *cis*-$[Co(en)_2(RCOO)_2]^+$. Thus, the success of the reaction of $[Co(en)_2CO_3]^+$ with a carboxylic acid ultimately depends on the acidity of the carboxylic acid. The ionization constants of the haloacetic acids range from 10^{-3} to 10^{-1} (e.g., $K_a = 5 \times 10^{-2}$ for $ClCH_2CO_2H$),[15] indicating that the haloacetic acids are relatively strong acids and should be substantially dissociated in water. This will drive eq 1 and 2 to the right, favoring formation of the product *cis*-$[Co(en)_2(RCOO)_2]^+$. However, $(CH_3)_3N\cdot BH_2COOH$ is a relatively weak acid ($K_a = 4.2 \times 10^{-9}$) and is not substantially dissociated in water.[5] Therefore, the analogous equilibrium involved in eq 1 lies to the left, and the overall reaction to form *cis*-$[Co(en)_2((CH_3)_3N\cdot BH_2COO)_2]^+$ does not occur to an appreciable extent.

Infrared Spectra. $(CH_3)_3N\cdot BH_2CO_2^-Na^+\cdot 0.25CH_3OH$ (1). The infrared spectrum of **1** differs markedly from that of the free acid, $(CH_3)_3N\cdot BH_2COOH$, and has been discussed elsewhere.[9] The pertinent point relevant to the reported assignments is that $(CH_3)_3N\cdot BH_2COOH$ shows a strong absorption at 1650 cm^{-1}, assigned to the carbonyl (C=O) stretching vibration[2], whereas in the spectrum of **1** this band disappears and two new bands appear at 1625 and 1450 cm^{-1}. The latter are assigned, respectively, to the antisymmetric and symmetric stretching vibrations of the carboxyl (COO) group.[16] The position of these bands in the spectrum of **1** as compared to their positions in the spectra of the metal complexes **2–5** allows the assignment of the coordination mode for the trimethylamine–boranecarboxylato ligand (**1′**) in each complex.

Cobalt(III). The infrared spectrum of the cobalt(III) complex (**2**) shows absorptions characteristic of O–H, N–H, C–H, B–H, and antisymmetric and symmetric COO stretching vibrations. The strong band at 1655 cm^{-1} is assigned to the antisymmetric COO stretching vibration, while the band at 1450 cm^{-1} is assigned to the symmetric COO stretching vibration. A band is not observed at 1485 cm^{-1}, which in trimethylamine–boranecarboxylato complexes of Fe(III) and Cr(III)[9] is assigned to the symmetric COO stretching vibration for a bridging bidentate ligand. The Δ value, assigned as the difference between antisymmetric and symmetric COO stretching frequencies, is 205 cm^{-1} for **2**, which is significantly greater than the Δ value observed for **1′** (175 cm^{-1}). It has been reported[17] that separations substantially greater than ionic are indicative of monodentate carboxylate coordination. In fact, virtually all acetato complexes that have $\Delta > 200$ cm^{-1} appear associated with monodentate coordination, a possible exception involving highly unsymmetrical bridging, i.e. "pseudo-monodentate" coordination.[18] On the basis of this infrared analysis, monodentate coordination is assigned for the trimethylamine–boranecarboxylato ligand in **2**. This conclusion is also supported by the stoichiometry of the reaction in that 2 mol of sodium chloride were recovered for every 2 mol of **1′** reacted, indicating that two ligands had replaced two chloride ions in *trans*-$[Co(en)_2Cl_2]Cl$.

Cobalt(II). The infrared spectrum of the cobalt(II) complex (**3**) exhibits absorption bands assigned to O–H, C–H, B–H, antisymmetric COO, symmetric COO, and covalent O–NO_2 stretching vibrations. The position of the antisymmetric and symmetric COO bands are again of particular importance in assigning a mode of coordination for **1′** in this complex. The strong band at 1618 cm^{-1} is assigned to the antisymmetric COO stretching vibration, while the strong and broad band at 1450 cm^{-1} is assigned as the symmetric COO stretching vibration, giving a Δ value of 168 cm^{-1}. The antisymmetric COO band in **3** appears at a lower frequency than that in the free ligand (1625 cm^{-1}), and the symmetric band stays the same. These values for the antisymmetric and symmetric COO bands relative to the free ligand rule out the possibility of a bidentate bridging coordination mode, where it is generally observed that both these bands increase relative to the corresponding bands in the free ligand.[17] A unidentate coordination mode is also ruled out on the basis of a Δ value of 168 cm^{-1}. However, the shifts of the antisymmetric and symmetric COO frequencies and the Δ value observed for **3** do not rule out a bidentate chelating coordination mode, and in fact, studies of the infrared spectra of haloacetate complexes show that

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a decrease in the antisymmetric COO stretching frequency relative to the free ligand is indicative of chelation.[19] Moreover, virtually all acetato complexes with Δ in the range 150–200 cm^{-1}, where the antisymmetric COO stretching frequency decreases relative to the free ligand, have chelating acetate groups.[19] In summary, the Δ value of 168 cm^{-1} and the decrease in the antisymmetric COO stretching vibration compared to the free ligand supports the assignment of a bidentate chelating coordination mode for the trimethylamine–boranecarboxylato ligand in **3**.

The infrared spectrum of **3** also reveals the absence of an antisymmetric $O-NO_2$ stretching band at 1380 cm^{-1}, a band corresponding to an electrostatically bound nitrate ion. Rather, the presence of bands at 1505 and 1290 cm^{-1} are noted, and these bands correspond to a covalently bound nitrate group.[20] The band at 1505 cm^{-1} is therefore assigned to the $O-NO_2$ antisymmetric stretching vibration since the analogous band occurs in the region 1530–1500 cm^{-1} for nitratopentaamminecobalt(III) complexes.[20] The band at 1290 cm^{-1} is assigned to the $O-NO_2$ symmetric stretching vibration on the basis that the analogous band occurs in the region 1290–1325 cm^{-1} in the nitratopentammine cobalt(III) complexes.

Calcium(II). The infrared spectrum of the calcium complex (**4**) exhibits the required O–H, C–H, B–H, antisymmetric COO, symmetric COO, and antisymmetric $O-NO_2$ (ionic) absorption bands. The strong band at 1620 cm^{-1} is assigned to the antisymmetric COO stretching vibration, while the strong and broad band at 1450 cm^{-1} is assigned as the symmetric COO stretching vibration, giving a Δ value of 170 cm^{-1}. The antisymmetric COO stretching band appears at a slightly lower frequency relative to that in **1′** (1625 cm^{-1}), and the position of the symmetric COO stretching band stays the same. This is the identical behavior observed for these bands in **3**. On the basis the same arguments given for the coordination of **1′** in complex **3**, a bidentate chelating coordination mode is also assigned to **1′** in **4**.

It is interestng to note the presence of the C=O stretching vibration for the acetone molecule in **4** at 1705 cm^{-1}. The "normal" carbonyl absorption frequency of a neat sample of acetone is 1715 cm^{-1}. Changes in the environment of the carbonyl can either raise or lower the absorption frequency from this "normal" value. In this case, the carbonyl stretching frequency is lowered, suggesting intermolecular hydrogen bonding between acetone and the water molecule from the complex, analogous to that occurring between a ketone and a hydroxylic solvent such as methanol where a slight decrease in the absorption frequency also occurs (e.g., a neat sample of methyl ethyl ketone absorbs at 1715 cm^{-1}, whereas a 10% solution of the ketone in methanol absorbs at 1706 cm^{-1}).[21]

Zinc(II). The infrared spectrum of the zinc complex (**5**) is somewhat unusual in that the position of the antisymmetric and symmetric COO stretching vibrations are quite different when compared with the position of these bands in **3** and **4**. The strong band at 1480 cm^{-1} is assigned to the antisymmetric COO stretching vibration, while the strong band at 1405 cm^{-1} is assigned to the symmetric COO stretching vibration. No absorption bands occur in the region 1600–1700 cm^{-1}. The value is only 75 cm^{-1} for this complex, which may be compared with a Δ value of 99 cm^{-1} for $Zn(CH_3CO_2)_2 \cdot 2H_2O$,[19] where the acetato ion behaves as a chelating ligand. On the basis of the observation that the antisymmetric and symmetric COO frequencies decrease in **5** relative to these frequencies for the free ligand and also on the basis of the similarity of the Δ values for **5** and $Zn(CH_3CO_2)_2 \cdot 2H_2O$, a chelating coordination mode for **1′** in complex **5** is concluded. An explanation of the small Δ value observed for **1′** in complex **5** is based upon coordination of the ligand to a small metal ion as is observed in the infrared data for a series of group 2 acetato complexes.[19] As the ionic radius of the metal (and subsequently the OCO angle) decreases for these acetato complexes, the Δ values also decrease. In fact, it was noted that even a slight change in the OCO angle will produce a substantial change in the difference between the two C–O stretching frequencies; e.g., when α-OCO = 5°, Δ = 44 cm^{-1}.[19] Therefore, the small Δ value for **5** may reflect a decrease of the OCO angle in **1′** upon coordination to the zinc(II) ion. Although this is a general phenomenon, it is not possible to say this is an absolute occurence since the correlation of small Δ values with small OCO angles does show an exception. The compound $Na[UO_2(O_2CCH_3)_3]$ has a very small Δ value (65 cm^{-1}) but has one of the largest OCO angles for a chelating acetato group.[18]

Table I. ^{11}B NMR Data for Compounds **1–5**

compd	solvent	δ	J_{B-H}, Hz
$(CH_3)_3N \cdot BH_2COOH$	D_2O	−10.2	97.5
1	D_2O	−8.75	92.7
2	CD_3CN	−9.44	95.2
3	CD_3COCD_3	−11.0	103
4	D_2O	−9.00	95.2
5	CD_3COCD_3	−9.68	97.6

Boron-11 and Proton NMR Spectra. The ^{11}B NMR chemical shifts of compounds **1–5** are listed in Table I. Only a 1:2:1 triplet, due to spin coupling of the two protons with the ^{11}B nucleus, is observed in the spectra of all the compounds. Some qualitative conclusions may be drawn by a discussion of the data in Table I.

The ^{11}B NMR chemical shift of **1** in water is −8.75 ppm vs. a chemical shift of −10.2 ppm for the parent acid, $(CH_3)_3N \cdot BH_2COOH$, in water. It should be noted that the ^{11}B NMR chemical shift for **1** in water is an average signal due to the exchange between the free anion (**1′**) and the acid, $(CH_3)_3N \cdot BH_2COOH$. The ^{11}B resonance has shifted downfield in **1**; i.e., the boron nucleus has become deshielded compared to the boron nucleus in the parent acid. This result appears to be inconsistent with the idea that an upfield shift of the ^{11}B resonance on ionization of $(CH_3)_3N \cdot BH_2COOH$ should occur since the carboxylato group is expected to be less electronegative than the carboxylic acid group. However, this apparently anomalous shift may be explained by nearest-neighbor anisotropic effects and is consistent with the ^{13}C shifts observed for the analogous organic carboxylic acids.[22] This anisotropic effect results from the deshielding experienced by the boron nucleus because of its orientation relative to the C=O bond and its distance from the carboxylato group.

The ^{11}B resonances of **2**, **4**, and **5** are also shifted downfield relative to that of $(CH_3)_3N \cdot BH_2COOH$. However, in these complexes, not only must anisotropic effects of the carbonyl group be considered but also inductive effects related to withdrawal of electron density from the boron nucleus by the positively charged metal ion. In contrast, the ^{11}B resonance of **3** is shifted upfield relative to that of $(CH_3)_3N \cdot BH_2COOH$, indicating that the boron nucleus has become more shielded in this complex. Moreover, the 1:2:1 triplet for **3** is broadened relative to the triplets observed for complexes **2**, **4**, and **5**. These effects observed for **3** are due, in part, to the alignment of the unpaired d electrons in the paramagnetic Co(II) ion with the magnetic field, which results in a low-energy configuration. An additional effect that contributes to the observed shielding occurs via interaction of the unpaired d electrons with the boron nucleus in **3** through the contact term of the Fermi-type Hamiltonian, an interaction that can be responsible for shifts on the order of 10 ppm.[21] Finally, the $^{11}B-^{1}H$ coupling constants listed in Table I indicate that the boron atom is four-coordinate in **1–5**. These coupling constants are consistent with the range of values observed for boron analogues of amino acids in general.[1-8]

Visible Spectra. Cobalt(III). The visible spectrum of **2** is shown in Figure 1, along with that of *trans*-$[Co(en)_2Cl_2]Cl$ for comparison. The configuration of the cation $[Co(en)_2((CH_3)_3N \cdot BH_2CO_2)_2]^+$ is assigned by a thorough analysis of these spectra and is consistent with the infrared spectral assignments. The two absorption bands found in the visible spectra of regular octahedral

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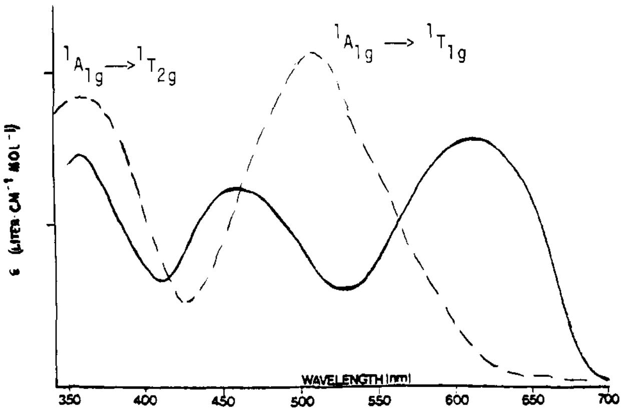

Figure 1. Visible spectra (0.02 M) of *cis*-$[Co(en)_2((CH_3)_3N{\cdot}BH_2CO_2)_2]^+$ (- - -) and *trans*-$[Co(en)_2Cl_2]^+$ (—) in water at 25 °C.

Table II. Visible Absorption Spectral Data of *cis*-$[Co(acetate)_2(en)_2]^+$ Complexes Compared with Those of *cis*-$[Co((CH_3)_3N{\cdot}BH_2CO_2)_2(en)_2]^+$ (**2**)

compd	band I, nm $^1A_{1g} \rightarrow {}^1T_{1g}$	band II, nm $^1A_{1g} \rightarrow {}^1T_{2g}$	
cis-$[Co((CH_3)_3N{\cdot}BH_2CO_2)_2(en)_2]^+$	515	364	151
cis-$[Co(CH_3CO_2)_2(en)_2]^+$	506	362	144
cis-$[Co(CH_2ClCO_2)_2(en)_2]^+$	501	361	140
cis-$[Co(CHCl_2CO_2)(en)_2]^+$	498	361	137
cis-$[Co(CCl_3CO_2)_2(en)_2]^+$	498	361	136

cobalt(III) complexes represent the transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. In complexes of the type CoA_4B_2 (e.g., *trans*-$[Co(en)_2Cl_2]Cl$ and **2**), which can exist in both cis and trans configurations, certain spectral features are diagnostic of either configuration. For complexes of this type it has been established both experimentally[23] and theoretically[24] that the first absorption band of the trans isomer splits significantly to give two bands, whereas that of the cis isomer does not. The origin of these features lies in the splitting of the $^1T_{1g}$ state by an environment of lower than O_h symmetry. Theory shows that splitting of the $^1T_{2g}$ state will always be slight, whereas the $^1T_{1g}$ state will be markedly split in the trans isomer whenever there is substantial difference in the positions of the ligands, A and B, in the spectrochemical series.[25] Such a difference is expected in the case with ethylenediamine and **1′**. Moreover, since the cis isomer lacks a center of symmetry it is expected to have a somewhat more intense spectrum than the trans isomer. These predictions are nicely borne out in Figure 1, which clearly shows that the first absorption band is not split and that the spectrum of *cis*-$[Co(en)_2((CH_3)_3N{\cdot}BH_2CO_2)_2]^+$ is more intense than that of *trans*-$[Co(en)_2Cl_2]Cl$, noting that comparable concentrations (0.02 M) have been used for both spectra.

A comparison of the visible spectral data obtained for a series of *cis*-(haloacetato)bis(ethylenediamine)cobalt(III) complexes[26] with analogous data for **2** (Table II) allows some conclusions to be drawn regarding the effect the BH_2^- group has on the carboxylate group in **1′**. Kuroda and Gentile[26] observed a decrease in the values for the first and second bands in the visible spectra as the halogen content in the haloacetato ligands increased. Both the haloacetato ligands and **1′** may be considered as π-donor ligands, which would induce antibonding character to the T_{2g} orbitals on the metal ion, resulting in the splittings observed for each complex. For example, the $-CCl_3$ derivative reduces the energy or size of the electron cloud on the carboxyl oxygen through an inductive effect, causing it to interact less with the metal than the carboxyl oxygen of the $-CH_3$ derivative; the antibonding consequence on the T_{2g} orbitals on the former is less thereby giving a larger Δ′ value (Table II). The largest Δ′ value observed for this series of structurally similar complexes belongs to **2**, indicating that the electron cloud on the carboxyl oxygen atom in **1′** is the largest of the group. This is expected due to the presence of the electron-releasing BH_2^- group and is also consistent with the trend in pK_a values observed for **1** and the haloacetate acids.

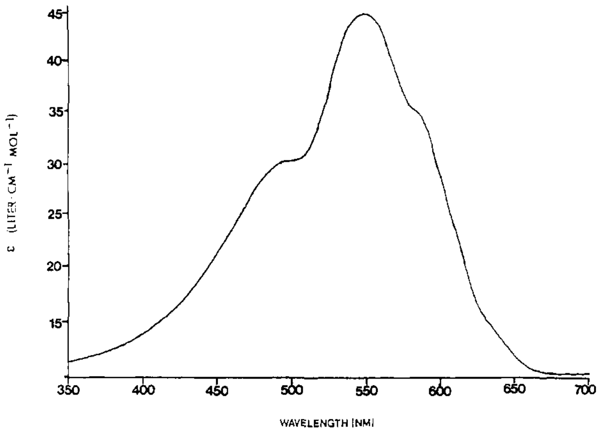

Figure 2. Visible spectrum of $Co((CH_3)_3N{\cdot}BH_2CO_2)NO_3{\cdot}CH_3CN{\cdot}3CH_3OH$ (**3**) in methanol at 25 °C.

Cobalt(II). The visible spectrum of the cobalt(II) complex (**3**) in methanol is given in Figure 2. The spectrum is similar to other spectra observed for octahedral cobalt(II) haloacetate complexes, which consist of a main absorption band around 540–550 nm, ($\epsilon \cong 0.45$ L mol^{-1} cm^{-1}) a strong shoulder around 480–490 nm, and a weak shoulder around 570–580 nm. The purple color of **3** indicates an octahedral configuration, based on the observation that octahedral cobalt(II) complexes are typically pale red or purple, whereas many common tetrahedral cobalt(II) complexes are an intense blue. On the basis of the comparatively low molar extinction coefficient of the principal absorption band, it is assumed that **3** has a trans (octahedral) configuration. This conclusion is based on the observation that cis octahedral bidentate nitrate complexes such as $Co[(CH_3)_3PO]_2(NO_3)_2$ give rise to an intense visible absorption ($\epsilon = 138$ L mol^{-1} cm^{-1}).[27]

The visible spectrum of **3** can be assigned in a manner consistent with its suggested structure. The free-ion ground term for cobalt(II) is ^4F with a ^4P term lying $15B$ to higher energy. Under the influence of an octahedral crystal field, it is expected that these levels split into $^4T_{1g}(F)$, $^4T_{2g}$, $^4A_{2g}$, and $^4T_{1g}(P)$, giving three spin-allowed transitions. In $Co((CH_3)_3N{\cdot}BH_2CO_2)NO_3{\cdot}CH_3CN{\cdot}3CH_3OH$ (**3**), four spin-allowed transitions occur due to a lifting of the degeneracy of the $^4T_{1g}(P)$ level to give two levels, $^4A_{2g}(P)$ and $^4E_g(P)$. Thus, two of the three peaks observed (545 and 486 nm) in the visible spectrum of **3** occur as a result of the tetragonal distortion of the geometry of the complex from regular octahedral symmetry. The peak at 545 nm is assigned to the $^4T_{1g}(F) \rightarrow {}^4E_g(P)$ transition, and the peak at 486 nm is assigned to the $^4T_{1g}(F) \rightarrow {}^4A_{2g}(P)$ transition. The remaining peak at 580 nm is assigned as the transition $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$. These assignments are consistent with those given for analogous haloacetate complexes of cobalt(II).[28]

Magnetic Susceptibility. Cobalt(II). The magnetic moment of **3** is 4.96 μ_B, which is within the accepted range of 4.7–5.2 for high-spin octahedral cobalt(II) complexes.[16] The spin-only value calculated for high-spin cobalt(II) is 3.87, arising from three unpaired electrons. The magnetic moments of these high-spin octahedral cobalt(II) complexes have a high orbital contribution because of the intrinsic orbital angular momentum in the octahedral ground state. This causes the moments to be in the 4.7–5.2-μ_B range. In addition, some octahedral cobalt(II) acetate

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complexes analogous to the distorted octahedral cobalt(II) boranecarboxylate complex (**3**) have been reported with magnetic moments in the range of 4.93–5.15 μ_B, similar to the one reported here.[29]

Summary

This study unequivocally supports the proposed formulation for complexes **2–5** showing that the trimethylamine–borane-carboxylato ligand (**1′**) behaves similarly to organic carboxylato ligands, acting as a monodentate (**2**) and bidentate chelating ligand (**3–5**). The biological activity of these compounds is currently under investigation.

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Polarized, Single-Crystal, Electronic Spectral Studies of $Cu_2Cl_6^{2-}$: Excited-State Effects of the Binuclear Interaction

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Variable-temperature, polarized, single-crystal, electronic spectra (10 000–45 000 cm^{-1}) have been taken on a series of mononuclear ($(CH_3NH_3)_2CuCl_4$, $(C_2H_5NH_3)_2CuCl_4$, and (N-(2-ammonioethyl)piperazinium)$CuCl_5{\cdot}2H_2O$) and binuclear ($KCuCl_3$, $(CH_3)_2NH_2CuCl_3$, and $LiCuCl_3{\cdot}2H_2O$) chlorocuprates in order to evaluate the excited-state effects of the binuclear cupric interaction. The increased intensity in the ligand field region of the binuclear complexes, relative to that of the monomers, has been shown to arise from the lower single-ion site symmetry in the dimer structure, which causes certain ligand field transitions to become parity allowed in a lower site symmetry. Attention is particularly focused on the absorption bands present in the dimers at ~20 000 cm^{-1}, which are not present in the analogous monomers, and the intensity, polarization, temperature dependence, and band shape of these "dimer" bands in the three binuclear cupric complexes have been studied in detail. We have experimentally evaluated the two possible assignments for these spectral features: simultaneous pair excitations (SPE; one photon excitation of ligand field transitions on both Cu(II)'s) and chloride-to-copper(II) charge-transfer transitions, which appear at 3700 cm^{-1} lower energy than in the analogous monomer. The temperature dependence of the dimer band intensity correlates with the population of the ground-state singlet, indicating that this is a singlet-to-singlet excitation. The polarization and, in particular, the band shape of this feature show that it should be assigned as the singlet component of a nonbonding π charge-transfer transition and not a SPE transition. The corresponding triplet-to-triplet excitation is estimated to have comparable intensity, yet it is not observed within the accessible spectral region below the intense charge-transfer cutoff. This charge-transfer triplet is thus required to be at least 3000 cm^{-1} to higher energy than the singlet. The large stabilization of this charge-transfer singlet, compared to that of the corresponding triplet, can be associated with a large antiferromagnetic excited-state exchange coupling relative to the ground-state exchange coupling in the binuclear complexes.

Introduction

The goal of numerous experimental[2] and theoretical[3] studies of binuclear Cu(II) complexes has been to explain the molecular ground-state properties resulting from the binuclear interactions. The observed antiferromagnetic or ferromagnetic behavior is usually described by a spin Hamiltonian involving exchange interaction between the Cu(II) valence electrons leading to a singlet ($S_{tot} = 0$) and a triplet ($S_{tot} = 1$) spin state. The molecular orbital or valence bond descriptions, however, generally include[3] configurational interaction between the ground state and a Cu(II) → Cu(II) charge-transfer excited state in order to achieve the experimentally observed sign and magnitude of the singlet–triplet splitting $2J$.

The binuclear interaction also has a direct effect on the excited states, as seen[4] in the optical spectra of binuclear Cu(II) complexes. While intensity enhancement of spin-forbidden ligand field transitions is well-known and studied in Mn(II)[5] and Cr(III)[6] dimers, the spin-allowed ligand field transitions of Cu(II) dimers are also observed to be more intense. Perhaps most striking is the appearance in the dimers of new transitions in a near-UV or visible spectral region that is transparent in the monomers. These dimer bands have generated a number of spectral studies and possible assignments, especially for the binuclear cupric carboxylate systems.[7] Finally, although not yet evaluated relative to the spectra of the monomers, the charge-transfer spectrum would also be expected to be strongly influenced by binuclear effects.

In order to experimentally characterize the effects of binuclear interaction on the excited states of copper(II) dimers, we have undertaken a detailed spectroscopic study of a series of binuclear chlorocuprates.[8] This series, containing a simple homogeneous ligand set, was chosen for a number of reasons. First, structurally characterized monomeric analogues exist for spectral comparison and their ligand field[9] and charge-transfer[10] spectra have been studied in detail through polarized, single-crystal methods. Second, while the dimer bands of binuclear Cu(II) complexes, such as

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