$$MnSO_4[B_{(MeOH)} - B_{(diox)}] = 109.0$$
$$MnBDS[B_{(MeOH)} - B_{(diox)}] = 106.0$$

That is, even though the dioxane baseline does not seem as good for the MnBDS, yet the difference between the dioxane and methanol results is essentially the same for the two salts.

This is probably enough speculation for the amount of data at hand. Before invoking the fickle aid of specific solvation effects further, data in a greater variety of solvent mixtures must be obtained. The aid of e.s.r. and ultraviolet–visible spectroscopy must be further enlisted; and an experimental attack on the problem of the viscosity correction must be made.

The authors feel, however, that a good case for the important role of selective solvation has been made. Moreover, the fact that a Mn(II) ion is very particular about its immediate surroundings should not be too amazing. The great recent success in the solution of the problems of transition metal chemistry by ligand field theory is based on this idea. In examining the solution chemistry of such ions, then, we can and should draw on the facts and techniques of the coördination chemists.

Acknowledgments.—The authors would like to express their gratitude to the National Science Foundation for financial support of this research. They also would like to thank Mr. Ronald Keyes for his invaluable aid with the computer calculations and Dr. Masatoki Yokoi for his experimental help throughout the work.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLORIDA]

Preparation and Infrared Studies of Metal Complexes Containing the Zwitterion Ligand Betaine, $(CH_3)_3\overset{+}{N}CH_2COO^-$

BY J. V. QUAGLIANO, S. KIDA AND J. FUJITA

RECEIVED APRIL 29, 1961

The reactions of the metal ions Co(II), Co(III), Ni(II), Cu(II) and Zn(II) with the zwitterion, betaine, $(CH_3)_3\overset{+}{N}CH_2COO^-$, have been studied. Coördination compounds of these metal ions have been prepared and their infrared spectra in the 2–15 μ region have been assigned. Comparison of the infrared spectra of these metal complexes with those of betaine and betaine hydrochloride reveals that the carboxylate ion antisymmetric stretching vibration at about 1630 cm.$^{-1}$ is retained, which in turn indicates that the resonance of the carboxylate group is maintained. The infrared spectra of metal complexes containing the monodentate betaine zwitterion are compared with those of the complexes of other amino acids such as glycine and alanine, previously reported, in which the amino acid ligands act as bidentate mononegative ions. The complexes, $[Co(NH_3)_5\{(CH_3)_3\overset{+}{N}CH_2COO^-\}](ClO_4)_3$ and $[Co(NH_3)_4\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_2](ClO_4)_3$, also have been prepared and the observed absorption bands of their infrared spectra have been assigned.

Introduction

In marked contrast to the extensive work that has been carried out on the preparation and studies of metal complexes in which the coördinating groups are neutral molecules (*e.g.*, H_2O, NH_3) or negative ions (*e.g.*, Cl^-, CN^-), relatively few investigations have been reported on metal complexes containing zwitterion ligands[1] and positive ion ligands.[2] The preparation and study of these latter two types of coördination compounds are being investigated in this Laboratory, and in this paper we report the preparation and infrared studies of some transition metal complexes with the simplest of the betaine zwitterion ligands namely $(CH_3)_3\overset{+}{N}CH_2COO^-$, which is in fact the betaine of glycine. The betaines are capable of donating methyl groups to other amino acids (transmethylation) and are also of considerable biological interest.

Coördination compounds of metal ions with the betaines should consist of the negative part of the zwitterion ligand orientated towards the central positive metal ion and the positive part orientated away from the metal ion. The resulting complex ion, which would have the net charge of the metal ion, then should be comprised of this ion surrounded by a sphere of negative charge and this in turn surrounded by a sphere of positive charge. Hence compounds containing zwitterion ligands coördinated with metal ions would be expected to show the general well-known properties associated with the more common type of coördination compound.

Experimental

Preparation of Compounds.—Betaine monohydrate, $(CH_3)_3\overset{+}{N}CH_2COO^-\cdot H_2O$ was supplied by K. and K. Laboratories, Inc., and was used without further purification.

Betaine (anhydrous) $(CH_3)_3\overset{+}{N}CH_2COO^-$ was prepared by heating the monohydrate to 110° in an oven. Its infrared spectrum showed the complete absence of water.

Tetrakis-(betaine)-Cu(II)-Perchlorate, $[Cu\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_4](ClO_4)_2$.—To a solution of 2 g. (0.0171 mole) of betaine monohydrate, $(CH_3)_3\overset{+}{N}CH_2COO^-\cdot H_2O$, in 30 ml. of absolute ethanol was added dropwise with stirring 1.6 g. (0.0043 mole) of $Cu(ClO_4)_2\cdot 6H_2O$ dissolved in 30 ml. of absolute ethanol. After standing, the deep blue crystals which formed were filtered, washed with absolute ethanol and dried in air. Recrystallization was effected by dissolving in the minimum amount of water followed by the addition of absolute ethanol. After about 5 hr. the crystals which formed were collected on a glass filter, washed with absolute ethanol and dried *in vacuo* over phosphoric anhydride. The crystals dissolve in water, but the original deep blue color immediately changes to the light blue color characteristic of aqueous solutions of the Cu(II) ion.

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[1] F. Lions, B. S. Morris and E. Ritchie, *J. Proc. Roy. Soc. N. S. Wales*, **76**, 294 (1942).

[2] See for example, J. C. Bailar, Jr., Ed., "Chemistry of the Coördination Compounds," Reinhold Publishing Corporation, New York, N. Y., 1956, p. 533.

All the metal complexes prepared containing betaine ligands only in the coördination sphere immediately change color on contact with water, indicating decomposition into the aquo metal complex and free betaine. The complexes, however, can be reformed by complete or nearly complete dehydration of the aqueous solution *in vacuo* over phosphoric anhydride.

Anal. Calcd. for $[Cu\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_4](ClO_4)_2$: Cu, 8.69; C, 32.86; H, 6.07. Found: Cu, 8.49; C, 32.98; H, 6.11.

Tetrakis-(betaine)-Cu(II) Nitrate, $[Cu\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_4](NO_3)_2$.—This compound was prepared and recrystallized by the same procedure as for the complex perchlorate described above, except 1.3 g. (0.0043 mole) of $Cu(NO_3)_2\cdot 6H_2O$ was used instead of copper(II) perchlorate. The deep blue crystals obtained, which had the identical color of the complex perchlorate salt, were dried *in vacuo* over phosphoric anhydride.

Anal. Calcd. for $[Cu\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_4](NO_3)_2$: Cu, 9.68; C, 36.61; H, 6.76. Found: Cu, 9.70; C, 36.62; H, 6.64.

The Light Green Copper(II) Complex of Empirical Formula $Cu\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_2Cl_2$.—To a concentrated aqueous solution containing 0.8 g. (0.0086 mole) of $CuCl_2\cdot 2H_2O$ was added slowly a solution of 2 g. (0.0171 mole) of betaine monohydrate dissolved in 30 ml. of methanol. The addition of 30 ml. of absolute ethanol to this clear, green solution resulted in the slow formation of a light green precipitate. This was filtered, washed with absolute ethanol and dried in air. Recrystallization from concentrated aqueous solution was effected by the addition of a 1:1 methanol-absolute ethanol solution. Light green crystals formed after the solution was stored in a refrigerator overnight. Attempts to prepare this compound using only alcoholic solutions resulted in the formation of gummy precipitates.

Anal. Calcd. for $Cu\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_2Cl_2$: Cu, 17.23; C, 32.56; H, 6.01. Found: Cu, 17.32; C, 32.40; H, 6.10.

The Dark Green Copper(II) Complex of Empirical Formula $Cu\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_2Br_2$.—Recrystallized dark green crystals of this complex were obtained by the method described above for the corresponding chloride, using $CuBr_2\cdot 2H_2O$ instead of $CuCl_2\cdot 2H_2O$.

Anal. Calcd. for $Cu\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_2Br_2$: Cu, 13.88; C, 26.24; H, 4.85. Found: Cu, 13.91; C, 26.41; H, 4.83.

Tetrakis-(betaine)-zinc(II) Nitrate, $[Zn\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_4](NO_3)_2$ was prepared by essentially the same procedure used in making the copper(II) nitrate complex, with a little modification. Since mixing of the reactants failed to give the zinc(II) complex immediately, it was necessary to keep the resulting nitrate solution in the refrigerator overnight. The white crystals which formed were dried *in vacuo* over phosphoric anhydride.

Anal. Calcd. for $[Zn\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_4](NO_3)_2$: Zn, 9.94; C, 36.51; H, 6.74. Found: Zn, 9.82; C, 36.27; H, 6.87.

Tris-(betaine)-zinc(II) Perchlorate, $[Zn\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_3](ClO_4)_2$ was prepared and recrystallized by the method described above for the tetrakis-(betaine)-copper(II) perchlorate, except that zinc(II) perchlorate was used instead of the corresponding copper(II) salt. White needle-like crystals were obtained on cooling the recrystallizing solution in a refrigerator overnight. Repeated preparations of this complex perchlorate always resulted in a 1:3 metal-to-ligand ratio.

Anal. Calcd. for $[Zn\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_3](ClO_4)_2$: Zn, 10.61; C, 29.24; H, 5.40; N, 6.86; Cl, 11.51. Found: Zn, 10.25; C, 29.30; H, 5.66; N, 6.67; Cl, 11.67.

The White Zinc(II) Complex of Empirical Formula, $Zn\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_2Cl_2$.—This white crystalline complex was prepared and recrystallized by the method used in making the tetrakis-(betaine)-copper(II) perchlorate complex.

Anal. Calcd. for $Zn\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_2Cl_2$: Zn, 17.64; C, 32.41; H, 5.99. Found: Zn, 17.98; C, 32.52; H, 6.03.

The Deep Blue Cobalt(II) Complex of Empirical Formula, $Co\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_2Cl_2\cdot 1/2H_2O$.—To 20 ml. of an aqueous solution containing 2 g. (0.017 mole) of betaine hydrochloride, $(CH_3)_3\overset{+}{N}CH_2COOH\overset{-}{Cl}$, was added an excess of solid cobalt(II) carbonate, 4 g., (0.029 mole). The mixture was heated with stirring on a steam bath until the evolution of carbon dioxide ceased and then filtered to remove the unreacted cobalt(II) carbonate. The filtrate which had the pink color characteristic of hydrated Co(II) salts was evaporated to dryness *in vacuo* over phosphoric anhydride. The deep blue crystals which resulted were washed with acetone and dried *in vacuo* over phosphoric anhydride. This complex is very soluble in absolute ethanol forming a deep blue solution. It is also very hygroscopic.

Anal. Calcd. for $Co\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_2Cl_2\cdot 1/2H_2O$: Co, 15.80; C, 32.20; H, 6.21. Found: Co, 16.35; C, 32.13; H, 6.61.

Betaine Complexes with Cobalt(II) Perchlorate.—Cobalt(II) perchlorate and betaine monohydrate form a pink hydrated complex in alcoholic solution. The pink compound, on heating to 100°, changes to a blue compound, and the reverse reaction readily occurs as the blue compound absorbs water from the atmosphere at room temperature. The analyses of a number of samples of these two complexes showed little consistency and revealed that a very slight change of preparative conditions greatly affects the composition of the complex formed. Infrared spectra showed the absence of water in all specimens of the blue compound. The spectra were, in fact, practically identical although analyses varied from the calculated 1:3 metal–ligand ratio to 1:4.

The blue compound used for detailed infrared study was obtained by heating at 100° the pink variety which had been prepared by the method for making the anhydrous Cu(II) complex, $[Cu\{(CH_3)_3\overset{+}{N}CH_2COO\}_4](ClO_4)_2$.

Anal. Calcd. for $[Co\{(CH_3)_3\overset{+}{N}CH_2COO\}_4](ClO_4)_2$: Co, 8.11; C, 33.07; H, 6.11. Found: Co, 8.19; C, 32.42; H, 5.96.

Betaine Complex with Nickel(II) Perchlorate.—Nickel(II) perchlorate and betaine form a light green complex. However, it is difficult to assign a definite formula to this compound since a number of samples prepared under identical conditions failed to yield concordant analytical results but did generally indicate approximately a 1:3 metal-ligand ratio.

The sample used for infrared study was obtained by the following method: To a saturated solution of 1 g. (0.0042 mole) of nickel(II) chloride dissolved in methanol was added a saturated methanol solution containing 3 g. (0.0257 mole) of betaine monohydrate. To the resulting green solution was added 0.5 g. (0.0047 mole) of lithium perchlorate, and absolute ethanol was added dropwise until the solution just became cloudy. The solution then was placed in the refrigerator and the light green complex which formed was filtered, washed with absolute ethanol and acetone and dried *in vacuo* over phosphoric anhydride.

Anal. Calcd. for $Ni\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_3(H_2O)(ClO_4)_2$: Ni, 9.36; C, 28.72; H, 5.63. Found: Ni, 9.96; C, 27.74; H, 5.55.

Betainepentamminecobalt(III) perchlorate, $[Co(NH_3)_5\{(CH_3)_3\overset{+}{N}CH_2COO^-\}](ClO_4)_3$, was prepared by adding excess betaine monohydrate, 5 g. (0.0428 mole) to 2 g. (0.0043 mole) of aquopentamminecobalt(III) perchlorate[3] dissolved in 20 ml. of water. The resulting solution was evaporated at 70° under reduced pressure to about half the original volume. On cooling, orange-pink crystals formed which were filtered, washed with a 1:1 water–ethanol mixture and then with absolute ethanol. This complex was recrystallized by dissolving in warm water, cooling in a refrigerator and drying *in vacuo* over phosphoric anhydride.

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[3] O. Hassel and G. B. Naess, *Z. anorg u. allgem. Chem.*, **174**, 24 (1928).

Anal. Calcd. for $[Co(NH_3)_5\{(CH_3)_3\overset{+}{N}CH_2COO^-\}](ClO_4)_3$: Co, 10.53; C, 10.73; H, 4.68. Found: Co, 10.90; C, 11.10; H, 4.70.

Bis-(betaine)-tetramminecobalt(III) Perchlorate, $[Co(NH_3)_4\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_2](ClO_4)_3$.—An aqueous solution of carbonatotetramminecobalt(III) perchlorate[3] was treated with an excess of aqueous perchloric acid added dropwise, and after the evolution of carbon dioxide ceased the solution was filtered. The dropwise addition of absolute ethanol to the filtrate resulted in the formation of purple diaquotetramminecobalt(III) perchlorate[4] which was filtered. The red-violet bis-(betaine)-tetramminecobalt(III) complex was obtained by the method described for the preparation and recrystallization of the betainepentamminecobalt(III) compound, using 1 g. (0.00217 mole) of the diaquotetramminecobalt(III) perchlorate and 5 g. (0.0370 mole) of betaine monohydrate.

Anal. Calcd. for $[Co(NH_3)_4\{(CH_3)_3\overset{+}{N}CH_2CO\overset{-}{O}\}_2](ClO_4)_3$: Co, 8.93; C, 18.20; H, 5.19. Found: Co, 8.60; C, 18.56; H, 5.04.

Whereas the metal complexes which contain betaine ligands only in the coördination sphere aquate immediately on coming into contact with water, the two Co(III) betaine-ammine complexes can be recrystallized from water. Furthermore, attempts to prepare complexes of trivalent cobalt, containing only betaine ligands, starting with cobalt(III) and betaine failed to produce stable complexes.

Deuteriated Betaine, $(CH_3)_3\overset{+}{N}CD_2COO^-$.—A sample of deuteriated betaine was supplied by Dr. L. J. Winters of this department. The nuclear magnetic resonance spectrum of the sample showed quite clearly that the hydrogen atoms of the CH_2 group only were exchanged.

Absorption Measurements.—All spectra were obtained with a Perkin-Elmer model 221 recording spectrophotometer using the potassium bromide disk technique[5] and checked by measurements in Nujol mulls.

Results

In Tables I, II and III are listed the infrared absorption frequencies and assignments of betaine, deuteriated betaine, betaine hydrochloride, betaine monohydrate and the betaine complexes of Cu(II), Zn(II), Co(II), Co(III) and Ni(II). The spectra of the copper(II) complexes were measured in Nujol and all others in KBr.

Discussion

General.—1. The CH Stretching Vibration Region.—The observed frequencies in the 3 μ region of the spectra of betaine and its Cu(II), Zn(II), Co(II), Co(III) and Ni(II) metal complexes arise from the CH(CH_3 and CH_2) stretching vibrations. In all the metal complexes studied the CH stretching vibrations appear, as expected, at practically the same frequency as in betaine. Upon deuteriation, the betaine band at 2976 cm.$^{-1}$ disappears whereas that at 3010 cm.$^{-1}$ remains unchanged. Consequently these bands can be assigned to CH stretching in the CH_2 (which deuteriates) and in the CH_3 groups, respectively. A significant difference appears in the 3 μ region of the spectrum of betaine monohydrate as compared with that of betaine. In the spectrum of the monohydrate, in addition to the CH group vibrations, the hydroxyl stretching vibration appears as a strong broad band at about 3300 cm.$^{-1}$. This OH frequency undoubtedly arises from the vibration of the weakly hydrogen-bonded H_2O molecule present only in betaine monohydrate. On the other hand, in the 3.5–4.5 μ region of the spectrum of betaine hydrochloride the OH stretching vibration appears as four very intense bands at 2703, 2632, 2488 and 2358 cm.$^{-1}$, together with some shoulders. These low frequency values indicate the presence of strong hydrogen bonding and probable dimerization in the solid state of betaine hydrochloride.[6]

2. The COO^- Antisymmetric Vibration.—In the spectrum of the free betaine ligand the very strong absorption band at 1621 cm.$^{-1}$ is assigned to the antisymmetric COO^- stretching vibration. Similar to the spectra of the amino acids studied[7] this absorption band is the most intense in the entire 2–15 μ region; it is sharper in betaine, $(CH_3)_3\overset{+}{N}CH_2COO^-$, than in the zwitterion amino acids containing a $\overset{+}{N}H_3$ or $\overset{+}{N}H_2R$ group, which groups also absorb in this region. In the spectrum of betaine monohydrate this band has its maximum again at 1621 cm.$^{-1}$ with several shoulders on the high frequency side. The position of this maximum and the presence of the shoulders support the conclusion that the water molecule in the monohydrate is only loosely bound. On the other hand, in the spectrum of betaine hydrochloride no absorption appears in this region, but a strong absorption is present at 1730 cm.$^{-1}$ and is assigned to the carbonyl (C=O) stretching vibration. The spectra of all the metal complexes exhibit an absorption at about 1630 cm.$^{-1}$ analogous to the 1621 cm.$^{-1}$ band of the free betaine ligand and assigned to the COO^- antisymmetric stretching vibration. Only slight differences in frequency appear in one complex compared with another. The closeness of all these frequencies to that of the free ligand indicates that the carboxylate group must involve only a small change in the electron distribution in the COO^- group. These data and conclusions are in agreement with previous communications describing the spectra of certain amino acids and their metal complexes.[8] However, in contrast to the greater shift (about 40 cm.$^{-1}$) to higher frequency values of the COO^- antisymmetric vibration reported in the spectra of the complexes of some metal ions; Pt(II), Pd(II), Co(III) with chelating amino acid ligands,[8] the corresponding shift in frequency in betaine complexes relative to betaine itself is very slight, being about 20 cm.$^{-1}$. In this respect the very slight shift in frequency of the COO^- antisymmetric stretching vibration to higher values upon coördination of the betaine zwitterion to Cu(II), Zn(II) and Co(II) resembles that in chelate glycine complexes of Ni(II) and Zn(II) but not that in the corresponding Pt(II), Pd(II) and Co(III) complexes,[8] which have been considered to be more covalent than the Ni(II) and Zn(II) complexes.

3. The COO^- symmetric stretching vibration of betaine is assigned to the band at 1394 cm.$^{-1}$ (this corresponds to the 1413 cm.$^{-1}$ frequency value for glycine). In the betaine–metal complexes this band shifts only very slightly to lower frequencies,

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[4] M. Linhard and M. Weigel, *Z. anorg. Chem.*, **260**, 65 (1949).

[5] M. M. Stimson and M. J. O'Donnell, *J. Am. Chem. Soc.*, **74**, 1005 (1952).

[6] See for example, W. Cochran, *Acta Cryst.*, **6**, 260 (1953).

[7] V. Moreno, K. Dittmer and J. V. Quagliano, *Spectrochim. Acta*, **17**, 1368 (1961).

[8] See for example, A. J. Saraceno, I. Nakagawa, S. Mizushima C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 5018 (1958).

TABLE I[a]

ASSIGNMENT OF THE OBSERVED FREQUENCIES IN CM.$^{-1}$ OF BETAINE, BETAINE HYDROCHLORIDE AND COPPER(II) BETAINE COMPLEXES[b]

Betaine	Deuteriated betaine	Betaine HCl	Betaine H_2O	Cu(bet)$_4$(ClO$_4$)$_2$	Cu(bet)$_2$Cl$_2$	Assignment
			3330s			OH str
3010sh	3012w	3010sh	3014w	3049m	2994m	CH str
				3003sh		
2976w		2967s	2979w	2959sh	2907m	
	2242w	2703s				
	2191vw CD str	2632s				OH str
	2142w	2571sh				
	2098w	2488s				
		2439sh				
		2358s				
		1767m sh				C═O str
(1718vw)		1730vs			1650sh	COO^- antisym str
					1637vs	
1621vs	1615vs		1621vs	1645vs	1504m	CH_3 deg def
1478m	1461m	1481s	1468m	1497m	1493m	CH_2 scissors
1439w		1461m	1450vw	1473s	1479m	
1414s sh	1419m	1441m sh	1421w	1458m	1445s	
				1425sh	1437s	CH_3 sym def
		1425m		1416sh	1416s	
		1412sh				C–O str and OH in plane def[b]
		1406s				
1403sh	1400sh		1400sh	1397vs	1397s	COO^- sym str
1394vs	1370vs		1380vs		1361s	
1334vs		1337w	1326s	1321vs	1328s	CH_2 wag
					1316s	
1239m	1259m	(1290w)	1241m	1238m	1238m	
		1247s			1214w	N–C str[b]
		1202vs				C–O str and OH in plane def[b]
1138vs		1134m	1145vw	1135sh	1139w	CH_3 rock and CH_2 twist[b]
1127w	1154m	1070m	1130m	1127sh	1130w	
	1088s CD_2 bend					
	1055m CD_2 wag			1101vs		
	1042sh			1080vs		
				1066s		ClO_4^-
1005w	1005sh		1008m	1006vw	1014w	CH_3 rock
980s	994s	992s	982s	985m	990m	
953m	970s	951m	952m	960m	964m	$\overset{+}{N}$–C str and C–C str[b]
931s	(938vw)	933m	931s	929vs	936s	CH_2 rock
897vs	902s	902s	891vs	906vs	902m	$\overset{+}{N}$–C str and C–C str[b]
	864m CD_2 twist	883vs				OH out of plane def[b]
	850w					
717m	686m		711m	779vw		
		778w			791w	
		677m COOH def			786w	
					746m	
		668sh			740m	COO def (bend, wag)[b]
				725m	715w	

[a] Abbreviations: s = strong; m = medium; w = weak; sh = shoulder; v = very. [b] These assignments are only tentative.

relative to betaine itself. A similar slight shift was reported for the chelate amino acid metal complexes.[8] In the metal complex of empirical formula, $Cu\{(CH_3)_3\overset{+}{N}CH_2COO^-\}_2\ Cl_2$, and the corresponding bromide complex, the absorption band assigned to the symmetric COO^- stretching vibration is split into two peaks at 1397 and 1361 cm.$^{-1}$, and 1395 and 1357 cm.$^{-1}$, respectively.

4. The 6.8 μ Region.—The CH_3 degenerate, the CH_2 bending and the CH_3 symmetric deformation vibrations occur in the 6.8 μ region. In the spectrum of betaine we may assign the bands at 1478 and 1439 cm.$^{-1}$ to the CH_3 degenerate and the CH_2 bending (or scissors) deformations respectively, on the basis of the assignments reported for trimethylammonium iodide[9] and glycine.[10] In the Cu(II), Zn(II), Co(II), Co(III) and Ni(II) metal complexes these two peaks are replaced by at least three peaks and these have higher frequency values. The in-

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(9) E. A. V. Ebsworth and N. Sheppard, *Spectrochim. Acta*, **13**, 261 (1959).

(10) M. Tsuboi, T. Onishi, I. Nakagawa, T. Shimanouchi and S. Mizushima, *ibid.*, **12**, 253 (1958).

frared absorption data for trimethylammonium iodide,[9] $H\overset{+}{N}(CH_3)_3I^-$, list two strong absorption peaks for the degenerate CH_3 deformation vibration at 1476 and 1460 cm.$^{-1}$ The CH_3 symmetric vibration in betaine may be assigned to the absorption band of medium intensity at 1414 cm.$^{-1}$; a similar band at 1401 cm.$^{-1}$ has been assigned to this vibration for tetramethylammonium iodide.[9] The spectra of the betaine metal complexes also show a similar absorption band at about 1420 cm.$^{-1}$

5. **The CH_2 Wagging Vibration.**—The CH_2 wagging vibration may be assigned to the strong, sharp band at 1334 cm.$^{-1}$ This assignment is supported by the fact that this band is shifted to 1055 cm.$^{-1}$ in the spectrum of deuterated betaine. Little change in profile and frequency takes place upon coördination of this zwitterion ligand to the metal ions studied. The glycino complexes of Pt(II) exhibit an absorption frequency at 1333 cm.$^{-1}$ for this vibration.[8]

6. **The CH_2 and CH_3 Rocking Vibrations.**—In the spectrum of glycine, $\overset{+}{N}H_3CH_2COO^-$, the CH_2 rocking vibration appears as a strong, sharp absorption at 910 cm.$^{-1}$,[10] and in the spectrum of betaine, a similar strong, sharp band is present at 931 cm.$^{-1}$ which disappears on deuteration. In the glycino *cis*- and *trans*-Pt(II) complexes this band shifts about 55 cm.$^{-1}$ to higher frequencies relative to glycine and becomes weak and broad. In contrast to this, however, the corresponding band in the Cu(II), Zn(II), Co(II), Co(III) and Ni(II) betaine complexes is practically unchanged in intensity, profile and frequency relative to betaine.

In the spectrum of betaine, the CH_3 rocking deformation vibrations are assigned to the very weak bands at 1138 and 1127 cm.$^{-1}$ (coupled with CH_2 twisting vibration), the very weak but sharp band at 1005 cm.$^{-1}$ and the strong, sharp band at 980 cm.$^{-1}$ As would be expected, there is practically no change in the shape and position of these bands in the metal complexes.

7. **The C–N and C–C Stretching Vibrations.**—The three sharp bands of the betaine spectrum at 1239, 953 and 897 cm.$^{-1}$ may be assigned to the $C\text{–}\overset{+}{N}$, and C–C stretching vibrations. The highest frequency band of medium intensity arises from the $C\text{–}\overset{+}{N}$ (probably doubly degenerate) stretching vibration; the medium intensity band at 953 cm.$^{-1}$ and the very strong band at 897 cm.$^{-1}$ are assigned to the $C\text{–}\overset{+}{N}$ stretching vibration and the C–C stretching vibration both of which couple with each other. In the spectrum of glycine the in-phase C–C–N stretching vibration appears at 893 cm.$^{-1}$, and as to be expected coördination of the donor nitrogen atom to the central metal ion of the complex changes this vibration only slightly. In the glycino Pt(II) complex, for example, the C–C–N in-phase stretching vibration increases to a frequency value of 921 cm.$^{-1}$ The C–C–N out-of-phase stretching vibration of glycine (1030 cm.$^{-1}$) would be expected to increase considerably when present in the glycino metal complexes. It appears at 1213 cm.$^{-1}$ in *cis* and 1247 cm.$^{-1}$ in *trans* bis-(glycino)-platinum(II). In contrast to the chelate character of the glycino ligand, which coördinates through the nitrogen atom and the COO^- group, the zwitterion betaine functions only as a monodentate group through the COO^- group. Consequently very little change in the $C\text{–}\overset{+}{N}$ and C–C stretching vibrations would be expected, and as the data in Tables I, II and III indicate, a maximum shift of only 10 cm.$^{-1}$ is observed.

TABLE II

ASSIGNMENT OF THE OBSERVED FREQUENCIES IN CM.$^{-1}$ OF ZINC(II) BETAINE COMPLEXES

$Zn(bet)_2Cl_2$	$Zn(bet)_4(NO_3)_2$	$Zn(bet)_2(ClO_4)_2$	Assignment
3030m	3012m	3049m	CH str
1634vs	1647vs	1650vs	
	1634vs	1617vs	COO^- antisym str
	1613vs		
1504m	1493m	1495m	CH_3 deg def
1481m	1475m	1477m	CH_2 scissors
1460m	1453sh	1453w	CH_3 sym def
1422m	1414m	1417m	
	1385vs		NO_3^-
1389vs	1364vs	1397s	COO^- sym str
1351s	1332s	1335m	
	1319sh	1317m	CH_2 wag
1235w	1238m	1244w	$\overset{+}{N}$–C str[b]
1130w	1126w	1176sh	CH_3 rock or CH_2 twist[b]
		1140vs	
		1117vs	ClO_4^-
		1086vs	
1004vw	1003vw	1006vw	CH_3 rock
978w	985m	985m	
955m	957m	957w	$\overset{+}{N}$–C str and C–C str[b]
	951m		
932m	931s	931m	CH_2 rock
901s	893s	896m	$\overset{+}{N}$–C str and C–C str[b]
	834m		NO_3^-
779w	(825vw)	781vw	
	779vw		COO^- def (bend, wag)[b]
728s	723m	723m	

8. **The COO^- Bending and Wagging Vibrations.**—In the spectrum of glycine the COO^- wagging vibration, which appears as a very sharp band at 694 cm.$^{-1}$, has a higher frequency[11] than the COO^- bending deformation vibration (607 cm.$^{-1}$). This is in contrast to all other amino acids previously reported.[9] On coördination of the glycino ligand the COO^- wagging vibration always shifts to a higher frequency, 752 cm.$^{-1}$ for bis-(glycino)-platinum(II) complex. In the spectra of the other amino acids reported[11] the COO^- bending vibration appears at the higher frequency and on coördination to metal ions is shifted to still a higher frequency.

In the 13–15 μ region of the spectrum of betaine only one band (717 cm.$^{-1}$) is observed which may be assigned to either the COO^- bending or wagging deformation vibration. However in the spectra of the Cu(II), Zn(II), Co(II), Co(III) and Ni-

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[11] See for example, K. Fukushima, *J. Chem. Soc. Japan*, **79**, 370, 1557 (1958).

TABLE III

ASSIGNMENT OF THE OBSERVED FREQUENCIES IN CM.$^{-1}$ OF COBALT(II), COBALT(III) AND NICKEL(II) BETAINE COMPLEXES

$Co(bet)_4$–$(ClO_4)_2$	$Co(NH_3)_5$-bet–$(ClO_4)_3$	$Co(NH_3)_4$-$(bet)_2$–$(ClO_4)_3$	$Ni(bet)_3H_2O$–$(ClO_4)_2$	Assignment
	3226vs	3175vs	3289 (OH str)	NH str
3106w				
2976w			2994sh	CH str
1645vs	1639s	1631vs	1650s	
			1634vs	COO^- antisym str
			1618s	NH_3 deg def
1504sh	1495m	1496s	1497m	CH_3 deg def
1499sh	1479m	1479s	1479m	CH_2 scissors
1484m	1420s	1466w, sh	1433s	CH_3 sym def
1456w		1414sh		
		1402s		
1396s	1401s	1385s	1408s	COO^- sym str
1351m			1346s	CH_2 wag
1324m				
	1337sh	1351s		
		1321s		CH_2 wag and NH_3[b]
	1318vs	1295s		Sym def
		1279m		
1239w	1247w	1239w	1238w	$\overset{+}{N}$–C str[b]
1205vw	1232w			
1117sh	1096vs	1144vs	1144v	
		1115vs	1111vs	ClO_4^-
1085vs		1081vs	1080vs	
1005vw	996w	(1008vw)	(1008vw)	
977w	986w	981w	980m	CH_3 rock
	(969vw)			
959w	958w	963m	962m	$\overset{+}{N}$–C str and C–C[b] str
933m	931m	933m	932m	CH_2 rock
	927m			
904m	909w	906m	903m	$\overset{+}{N}$–C str and C–C[b] str
	848s	859m		NH_3 rock
		831sh		
783vw		795sh	781vw	
		789m		COO^- def (bend, wag)[b]
	739m	745m		
726m	721sh	733m	725m	

(II) betaine complexes two absorption bands (and in some cases three) appear in this region. The higher frequency band may be assigned to the COO^- bending vibration (which with the exception of glycine, always appears at a higher frequency than the wagging vibration) and the lower band to the COO^- wagging vibration.

Assignment of the Observed Frequencies Corresponding to the Stretching and Deformation Vibrations of the Coördinated NH_3 Molecule in Betaine–Ammine Complexes of Co(III).—Previous investigations have shown that the absorption peaks in the 3 μ region associated with the H–N stretching vibrations of coördinated NH_3 molecules shift to lower frequencies on formation of the nitrogen-to-metal bond.[12] Furthermore, an increase in total absorption in the 3 μ region also accompanies the formation of this bond. The spectra of betaine–ammine Co(III) complexes are in agreement with these observations. Assignments of the observed H–N frequencies in this region are given in Table III.

Extensive spectral (2–15 μ region) and theoretical studies have been carried out on the coördinated NH_3 deformation vibrations and the positions, profiles and relative intensities of the three ensuring bands have been discussed.[12] In Co(III) complexes the relatively weak, broad, but symmetrical band at about 1600 cm.$^{-1}$, the very sharp, intense band at about 1300 cm.$^{-1}$ and the very broad, medium and symmetrical band at about 850 cm.$^{-1}$ have been assigned to the degenerate, symmetric and rocking vibrations, respectively, of the coördinated NH_3 ligand.

Comparison of the spectra of betaine–ammine metal complexes on the one hand with those of betaine and the betaine metal complexes on the other reveals overlapping of the NH_3 degenerate vibration band with the COO^- antisymmetric stretching vibration band and also of the NH_3 rocking vibration with the COO^- bending vibration band, but in each case the NH_3 deformation absorptions can be recognized easily. Assignments of these three absorption bands in the spectra of the betaine–ammine Co(III) complexes are given in Table III.

The solubility in various suitable solvents of the complexes discussed above was examined with a view to determining their conductivities and hence obtaining data on their configurations. However, satisfactory results were obtained in the case of three of the complexes only, the others being insoluble. The conductivities (ohm^{-1} cm.^{2} mole^{-1}) in 10^{-3} molar solution in dimethylformamide in the three instances were, $[Co\{(CH_3)_3{}^+NCH_2COO^-\}_4](ClO)_4)_2$: 192.0; $Ni\{(CH_3)_3{}^+NCH_2COO^-\}_3H_2O(ClO_4)_2$: 189.5; $[Zn\{(CH_3)_3{}^+NCH_2COO^-\}_3](ClO_4)_2$: 168.0. By analogy with similar work by Tyree, *et al.*,[13] on the complexes of pyridine-N-oxide, it may be concluded that the above complexes are 2:1 electrolytes.

Acknowledgments.—We are thankful to Dr. I. Nakagawa for a helpful discussion in the interpretation of the infrared spectra. This investigation was supported in part by research grant, A-2734, of the Public Health Service, Department of Health, Education and Welfare, National Institutes of Health, and the U. S. Atomic Energy Commission AT-(40-1)-2503.

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[12] G. F. Svatos, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, **77**, 6159 (1955).

[13] J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley and S. Y. Tyree, *ibid.*, **83**, 3770 (1961).