

molecular structure, although a crystallographic phase change is not involved. The sharp increase of the magnetic moment with rising temperature thus indicates the transition of a potential barrier between the two molecular configurations,⁵⁵ the character of which may only tentatively be described at present.⁴² The activation energy of the transition can be estimated at $\Delta E_A = 120 \text{ cm}^{-1}$ (about 350 cal/mole) for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and at 160 cm^{-1} (about 460 cal/mole) for $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$.

The transition ${}^1A_1(t_2^6) \rightarrow {}^5T_2(t_2^4e^2)$ involves the transfer of two electrons from a t_2 to an e orbital which should be followed by a marked increase in the ionic radius of about 0.2 Å.^{50,56,57} In addition, the low-spin

(55) The number of molecules undergoing such transition may be affected to some extent by the defect structure of the solid, thus providing an explanation for the different low-temperature moments encountered in differently prepared samples.

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d^6 configuration involves the filled t_2 subshell and is thus particularly stable (ligand field stabilization 2.4Δ as compared to 0.4Δ for the high-spin configuration). Thus it is not unreasonable to assume that spin-state equilibria in compounds of the d^6 configuration are *in general* associated with a change in molecular dimensions. Further investigations on this problem are in progress.

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Raman Study of Glycine Complexes of Zinc(II), Cadmium(II), and Beryllium(II) and the Formation of Mixed Complexes in Aqueous Solution¹

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Raman spectra are reported for the aqueous systems zinc(II)-glycine, cadmium(II)-glycine, and beryllium(II)-glycine in the pH range 2.0–7.0. At the lower pH range, glycine forms monodentate complexes with the metal ions, through the oxygen atom of the carboxyl group. At the higher pH range, glycine forms mono, bis, and tris bidentate complexes with Zn(II) and Cd(II) ions. However, at higher pH, glycine does not bind the Be(II) ion, and for this system, glycine does not seem to form a bidentate complex with beryllium. Spectra of the system ZnCl_2 -glycine at pH 5.0 indicate the presence of at least two mixed complex species involving bidentate glycine and the chloride ion bound to the metal. The system CdCl_2 -glycine at pH 5.0 also contains a mixed complex species. These systems at low pH contain mixed species containing monodentate glycine and chloride ions bound to the metal ions. Spectra of systems Zn(II)-glycine- SCN^- and Cd(II)-glycine- SCN^- at pH 5.0 indicate the presence of at least two mixed complex species containing bidentate glycine and one and two thiocyanate ions bound to the metal. Finally, the spectra of the systems ZnCl_2 -glycine- SCN^- and CdCl_2 -glycine- SCN^- at pH 5.0 seem to indicate the presence of a ternary complex containing bidentate glycine, chloride, and the thiocyanate ions bound to the metals.

The Raman spectra in solution of glycine in its various protonated forms have been the subject of numerous investigations.^{2–4} The infrared spectra of glycine in aqueous solutions have been reported by Nakamoto, *et al.*,⁵ who have also studied the solution spectra of some metal complexes of amino acids. Detailed vibrational normal coordinate analysis of glycine⁶

and its 1:1 metal complex⁷ have also been reported in the literature. Infrared spectra in the solid state of a variety of metal-glycino complexes have also been studied by a number of investigators.^{8–12} To date, however, Raman spectra of metal-glycino complexes have not been investigated. The present study concerns the Raman spectra in aqueous solution of some zinc(II)-glycine complexes and includes mixed complexes of zinc glycinate with chloride and thiocyanate

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TABLE I
 RAMAN SPECTRA (cm^{-1}) OF GLYCINE AND GLYCINE-ZINC(II) SOLUTIONS AT VARIOUS pH^a

$\text{H}_2\text{NCH}_2\text{COO}^-$ ^b	$^+\text{H}_3\text{NCH}_2\text{COO}^-$ ^b	$^+\text{H}_3\text{NCH}_2\text{COOH}^b$	Zn(II)-glycine ^c (pH 2)	Zn(II)-glycine ^c (pH 5)	Assignments ^d
507 m	502 m	494 m	500 s	520 m	CO_2^- rock; NH_3^+ torsion
575 w	577 w	...	580 vw	570 vw	CO_2^- wag
...	665 w	644 w	670 vw	660 vw	CO_2^- scissor
899 m	896 s	869 s	902 vs	918 s	C-C str
968 w	955 w, sh	CH_2 rock?
...	1027 m	1042 m	1030 m	1050 w	C-N str
1100 m	1118 m	1123 w	1110 m, b	1100 w	NH_2 twist; NH_3^+ rock
1169 w	1175 vw	1180 vw	CH_2 twist
1315 m	1310 m, sh	NH_2 wag?
1343 s	1327 s	1308 s	1335 s	1340 s	CH_2 wag
1407 vs	1410 s	...	1418 vs	1400 s	CO_2^- sym str
1440 sh	1440 m	1433 m	1440 s, sh	1445 m	CH_2 scissor
1611 vs	1615 s	1644 vs	1610 m	1600 m	CO_2^- antisym str
...	...	1744 s	C=O str
...	2879 w	CH_2 str
2935 vs	2968 s	2975 vs	2975 vs	2945 vs	CH_2 str
...	3011 m	3011 s	3015 s	2975 m, sh	CH_2 str
3320 m	3300 m, b	NH_2 str
3385 m	NH_2 str

^a s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder. ^b Values taken from ref 4. ^c Values are for equimolar (2 M) solutions. Only the ligand frequencies are tabulated. ^d According to ref 6.

ions. In addition, experiments are reported for cadmium and beryllium complexes with glycine.

Experimental Section

Spectra were recorded with a Cary Model 81 Raman spectrophotometer using the 4358-A line of Hg for excitation. The glycine solutions were found to be slightly fluorescent. This difficulty was overcome for the neutral and acidic solutions, by treating the solutions with Norit A and filtering through a fine filter.

For many of the experiments, intensity measurements were required. For these, each solution contained a known concentration of NO_3^- which served as internal standard. For this purpose, the intensity of the Raman line in question was compared with that of the A_1 line of NO_3^- which appears at 1050 cm^{-1} . For such measurements, the tube was surrounded with a polaroid cylinder which admitted light polarized perpendicular to the axis of Wood's tube. For determining degree of depolarization, this cylinder was replaced by one which admitted light polarized parallel to the tube axis.

All reagents were AR grade except for some of the glycine. It was found that identical spectra were obtained for reagent grade glycine, recrystallized, and for "purified reagent" (Eastman).

Results

The Raman spectrum of glycine undergoes some marked changes when the zinc(II) ion is introduced into the solution, indicating complexation of the ligand. At lower pH (ca. 2.0) Raman spectra of Zn(II)-glycine solutions resemble that of the glycine dipolar ion. As the pH is increased, the spectrum changes considerably, almost all of the ligand lines being shifted in position. In Table I are summarized the Raman spectra of the ligand in its various ionic forms as reported by Ghazanfar, *et al.*,⁴ and the spectra of the Zn(II)-glycine solutions of pH 2 and 5. The last two solutions are for equimolar Zn(II)-glycine solutions. These latter solutions also show new low-frequency Raman lines. If lithium chloride is added to these solutions, a line appears at 287 cm^{-1} , characteristic of the Zn-Cl stretching vibration;¹³ if sodium thiocyanate

is added to these solutions, the spectrum of the thiocyanate (2100 and 820 cm^{-1}) is characteristic of coordinated SCN^- ion as opposed to "free" SCN^- (2068 and 747 cm^{-1}). Also, solutions containing various ratios of glycine to zinc (without Cl^- or SCN^-) yield almost identical spectra, except at the lower frequencies; a line at 445 cm^{-1} for equimolar Zn(II) and glycine shifts to 425 cm^{-1} as the ratio of glycine to Zn(II) is increased. An interpretation of these data and those for solutions containing Cl^- and SCN^- is given in the following section, with data plotted in Figures 1 and 2. Data obtained for solutions containing cadmium and beryllium salts in place of zinc are also discussed.

Discussion

As can be seen from Table I, the spectra of the three ionic forms of glycine are quite distinctive and can be used to identify the protonation site in glycine. Table I also lists the vibrational assignments of the ligand, as given by Suzuki, *et al.*,⁶ for the dipolar ion.

Spectra of Zinc Nitrate-Glycine Solutions.—The Raman spectra of solutions containing various mole ratios of zinc nitrate and glycine are all practically identical. They are also very similar to the spectrum of the free ligand. The pH of these solutions was near 2.0. That the carboxylic group is not protonated in these solutions is shown by the absence of the C=O stretching frequency at 1743 cm^{-1} and by the absence of the C—C stretching frequency at 869 cm^{-1} . The C—H stretching frequencies and also the spectrum in the region 1300 – 1600 cm^{-1} are characteristic of the dipolar ion, indicating that the amino group is protonated. The main difference between the spectra of the zinc nitrate-glycine solutions and the glycine dipolar ion is in the shifting of the C—C stretching

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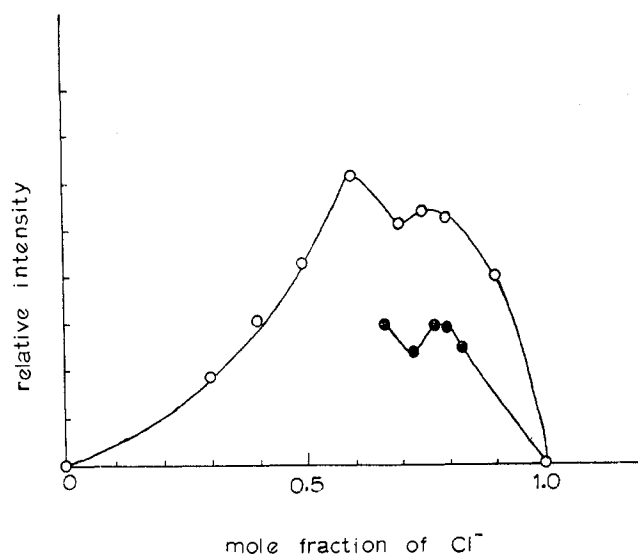


Figure 1.—Plot of the peak height at 287 cm^{-1} vs. the mole fraction $[\text{Cl}^-]/\{[\text{ZnGly}^+] + [\text{Cl}^-]\}$. Open circles refer to the system $\text{Zn}(\text{NO}_3)_2$ -glycine- Cl^- , and filled circles, to the system ZnCl_2 -glycine- Cl^- .

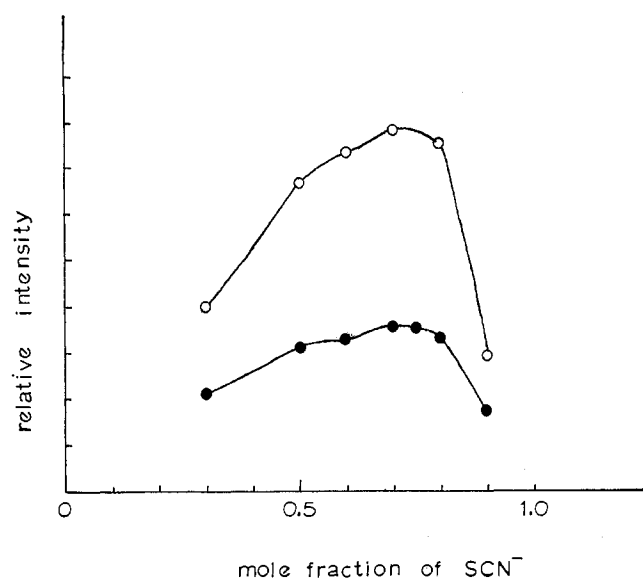


Figure 2.—Plot of the peak height at 2100 cm^{-1} vs. the mole fraction $[\text{SCN}^-]/\{[\text{ZnGly}^+] + [\text{SCN}^-]\}$. Open circles refer to the system ZnCl_2 -glycine- SCN^- , and filled circles, to the system $\text{Zn}(\text{NO}_3)_2$ -glycine- SCN^- .

frequency to 902 cm^{-1} . This is taken to indicate that the glycine is coordinated to the metal ion. By measuring the height of the peak at 902 cm^{-1} in a series of solutions containing varying proportions of zinc nitrate and glycine, keeping the total concentration constant (the classical Job method of continuous variation^{14,15}), a curve was plotted of the height at 902 cm^{-1} vs. the mole ratio of glycine to zinc. The curve obtained shows broad inflection corresponding to the solution containing the mole ratio of glycine to zinc near 2. The curve, however, does not show a well-developed maximum, because the free glycine line at 896 cm^{-1} is intense and badly overlaps that for bound

glycine. This increases the intensity of the 902 cm^{-1} Raman line at higher glycine concentrations. However, the fact that the curve does show an inflection and the fact that the intensity of this Raman line undergoes marked change on introduction of the metal ion tend to confirm the conclusion that the glycine is coordinated to the metal ion. Since the amino group is protonated, it must be concluded that the glycine is bound only through the oxygen atom of the carboxylic group. These solutions show a very weak Raman line at 395 cm^{-1} , which is not present in the glycine spectrum. This is probably due to a Zn-O stretching vibration.

When the pH values of the zinc nitrate-glycine solutions are raised to the range between 3 and 8, the spectrum of the ligand changes from that corresponding to the dipolar ion to that corresponding to the anion. Since the free ligand in this pH range is in the form of the dipolar ion, the deprotonation of the amino group in the presence of zinc ion points strongly to the formation of a Zn-N bond; or, in other words, the glycine acts as a bidentate ligand in this pH range. If the pH is raised further, precipitation occurs in these solutions. The precipitate can be redissolved by adding an excess of alkali, and the spectrum of the clear solution so obtained is characteristic of free glycine anion and of the zincate ion.

Hence, the pH range characteristic of bidentate linkage by the ligand is between 3 and 8 (the higher limit can be extended in solutions which contain a large excess of glycine). As mentioned previously, the ligand spectrum is characteristic of the glycine anion, but all of the frequencies of the free anion undergo shifts by 10 or more wavenumbers, and, hence, the coordinated ligand can be readily identified. The C-C stretching frequency, for example, shifts from 896 to 915 cm^{-1} . Also, in these solutions, a new polarized Raman line appears at 445 cm^{-1} . Since the latter line is not present at lower pH where the nitrogen is protonated, it can be assigned to Zn-N stretching vibrations. The frequency of the Zn-N stretching vibration in these glycine complexes compares favorably with the Zn-N stretching frequency in the zinc complexes of ethylenediamine¹⁶ and ammonia.¹⁷ The very weak Raman line around 395 cm^{-1} , which was observed in the zinc nitrate-glycine solution of pH 2, still persists in the solutions at higher pH and can be assigned to Zn-O stretching vibration.

The spectrum of the coordinated ligand does not change much with varying proportions of zinc nitrate and glycine except for the C-C stretching frequency, which moves from 918 cm^{-1} for the equimolar zinc-glycine solution to 912 cm^{-1} for the solution having the ratio of glycine to zinc of 3. The line around 450 cm^{-1} changes in position as the mole ratio of glycine to zinc is changed. An attempt was made to draw a Job plot for the zinc nitrate-glycine system in this pH range (3-8). However, owing to problems of precipitation,

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it was possible to maintain the total concentration of zinc(II) plus glycinate ion only approximately constant. The plot made under these circumstances, for the height of the peak around 915 cm^{-1} , showed three maxima. This probably indicates that there are at least three species formed, having ratios of glycine to zinc of 1, 2, and 3. The plot for the height of the lower frequency peak at 460 cm^{-1} showed a maximum around the ratio of glycine to zinc of 1. The plot for the height at 430 cm^{-1} showed a prominent peak around a value for the ratio of 2, and the plot for the height at 420 cm^{-1} showed some indications for a peak around 3. Apparently, there are three species formed: a monoglycino complex with a Zn-N stretching frequency, *ca.* 445 cm^{-1} , the bis complex, *ca.* 430 cm^{-1} , and the tris complex, *ca.* 425 cm^{-1} . For the last case, there is another much weaker line at 150 cm^{-1} , which may arise from a chelate-ring bending vibration, the numbers being obtained from the spectra of solutions containing the corresponding mole ratios of glycine to zinc.

From the solution containing the mole ratio of glycine to zinc of 2, at pH 6.0, crystals of $\text{Zn}(\text{NH}_2\text{CH}_2\text{COO})_2 \cdot \text{H}_2\text{O}$ can be precipitated and the infrared spectrum of this compound is identical with that reported by Saraceno, *et al.*⁹ According to Low, *et al.*,¹⁸ $\text{Zn}(\text{NH}_2\text{CH}_2\text{COO})_2$ in this crystal is planar, with the glycine assuming *trans* configuration around the metal ion. The Raman spectrum of this solid was recorded, and it showed a Raman line of medium intensity at 470 cm^{-1} . The Raman spectrum of these crystals dissolved in water, however, showed no Raman line at 470 cm^{-1} , but at 430 cm^{-1} , which has been assigned to the Zn-N stretching vibration. This shift of the Zn-N frequency from 470 cm^{-1} in the solid to 430 cm^{-1} in solution may be due to solid-state interactions or, more probably, to the fact that the bis(glycino)-zinc(II) complex which is planar in the solid, with bridging carboxylates, converts to a simple, tetrahedral configuration in solution.

Zinc-Glycine-Chloride System.—When lithium chloride is added to a solution containing equimolar quantities of zinc nitrate and glycine in the pH range 3–6, in addition to the lines characteristic of coordinated glycine, a polarized Raman line appears at 287 cm^{-1} . This line corresponds to a Zn-Cl stretching vibration.¹³ To investigate the species formed, the Job method was again used. One of the stock solutions used was a 2.86 *M* solution of lithium chloride. The other solution contained 2.86 moles of zinc nitrate and 2.86 moles of glycine at pH 5.0. By mixing various proportions of the two solutions, keeping the total volume always constant, the heights of the Raman line due to Zn-Cl stretching vibration at 287 cm^{-1} were measured. The Job plot was then made on the assumption that all of the zinc present in the original stock solution was in the form of the monoglycinozinc complex and is reproduced in Figure 1. As can be seen, the curve shows two maxima, corresponding to the mole ratios of chloride

to zinc of 1.5 and 3.0. Another Job plot was drawn for the peak height of the 287-cm^{-1} Raman line, using, as one of the stock solutions, a solution of lithium chloride and, as the other, a solution containing zinc chloride and glycine at pH 5.0. This curve also shown in Figure 1 is very similar to the one mentioned above. The plots clearly indicate that there are at least two different chloro complexes formed between chloride and zinc. Because of the necessary assumption of ideal solutions and overlapping frequencies, the formulation is not clear. One species may contain either one or two chlorides per zinc, and the other, two or more. For all of these solutions, it was verified that the glycine was also coordinated to zinc. Now, it is possible that the glycine is coordinated to zinc, not as a monoglycino complex, but as a bisglycino complex. In that case, the chloride ions may simply be coordinated to zinc alone and not take part in a mixed complex with glycine. To decide this question, two solutions were prepared, one containing equimolar quantities of ZnCl_2 and glycine at pH 5.0 and the other containing a mole ratio of glycine to ZnCl_2 of 2 at pH 5.0. It was found that the latter solution, even though it was five times more dilute than the former, yielded crystals corresponding to $\text{Zn}(\text{NH}_2\text{CH}_2\text{COO})_2 \cdot \text{H}_2\text{O}$. The increased solubility in the former solution makes it seem highly probable that the solution indeed contains a mixed complex species and not merely $\text{Zn}(\text{NH}_2\text{CH}_2\text{COO})_2$ and ZnCl_4^{2-} . Furthermore, the Zn-Cl stretching frequency for tetrachlorozincate is 278 cm^{-1} , different from the value for our solutions.

A solution containing equimolar quantities of ZnCl_2 and glycine at pH 5.0 shows a Raman line corresponding to Zn-Cl stretching vibration. However, the solutions containing mole ratios of glycine to ZnCl_2 of 2 and 3 do not show this Raman line. If the bis(glycino)-zinc complex species were tetrahedral in solution, as was suggested previously, it would not be possible for the chloride ions to coordinate to the metal without a drastic change of geometry.

However, solutions of pH less than 2, containing 1:2 mole ratios of ZnCl_2 and glycine, showed the Raman line at 287 cm^{-1} , further confirming the monodentate binding by glycine in these species. Coupled with the earlier observation of an inflection in the Job plot corresponding to the ratio of glycine to zinc of 2, this observation points to the probable existence of a mixed complex species, $\text{Zn}(\text{NH}_2\text{CH}_2\text{COO})_2\text{Cl}_2$, having monodentate glycine.

Zinc-Glycine-Thiocyanate Systems.—Just as in the case of the chloride, when sodium thiocyanate is added to an equimolar solution of zinc nitrate and glycine, the Raman spectrum shows that the thiocyanate is also bound to the metal. Again, two Job plots were drawn, using thiocyanate as one standard solution and two other solutions, one containing equimolar zinc nitrate and glycine and the other, equimolar zinc chloride and glycine, the pH of the latter solutions being 5.0. The free thiocyanate lines at 747 cm^{-1} (C—S stretching) and at 2068 cm^{-1} (C≡N stretching) are

(18) B. W. Low, F. L. Hirshfeld, and F. M. Richards, *J. Am. Chem. Soc.*, **81**, 4412 (1959).

shifted on coordination to 820 cm^{-1} and *ca.* 2100 cm^{-1} , respectively. The Job plots were drawn for the height of the peak at 2100 cm^{-1} . Figure 2 shows the curve obtained using ZnCl_2 -glycine and also that obtained using $\text{Zn}(\text{NO}_3)_2$ -glycine. The two curves are very similar and show maxima corresponding to the ratios of SCN^- to zinc of about 1 and 2.

When the Raman spectrum of the solution containing equimolar quantities of zinc nitrate, glycine, and sodium thiocyanate at pH 5.0 is recorded, the $\text{C}\equiv\text{N}$ stretching frequency is at 2110 cm^{-1} . As more sodium thiocyanate is added to the solution, this frequency moves down to 2100 cm^{-1} . It is probable then that the $\text{C}\equiv\text{N}$ frequency at 2110 cm^{-1} is characteristic of a species containing one thiocyanate ion and that at 2100 cm^{-1} is characteristic of the species containing two thiocyanate ions.

When the Raman spectrum of the solution containing equimolar quantities of ZnCl_2 , glycine, and sodium thiocyanate at pH 5.0 is recorded, it shows the $\text{C}\equiv\text{N}$ stretching frequency to be 2100 cm^{-1} . However, the $\text{Zn}-\text{Cl}$ stretching frequency which occurs at 287 cm^{-1} when no thiocyanate is present is shifted down to 275 cm^{-1} . As more thiocyanate is added, the $\text{C}\equiv\text{N}$ stretching frequency does not shift, but the Raman line due to the $\text{Zn}-\text{Cl}$ stretching vibration loses intensity and disappears altogether. In all of these spectra, the glycine is coordinated, and the Raman line at 915 cm^{-1} arising from $\text{C}-\text{C}$ stretching vibration does not lose any intensity. Since it was concluded that the chloride ion forms a mixed complex with zinc and glycine, the observations made here can be explained by assuming that the thiocyanate first replaces one and then both the chlorides. In other words two mixed complex species $\text{Zn}(\text{NH}_2\text{CH}_2\text{COO})\text{SCNCl}^-$ and $\text{Zn}(\text{NH}_2\text{CH}_2\text{COO})(\text{SCN})_2^-$ are formed. In the chloride-free solutions, when the $\text{C}\equiv\text{N}$ stretching frequency is present at 2110 cm^{-1} (different from the solutions containing chloride ions), there is probably the complex species $\text{Zn}(\text{NH}_2\text{CH}_2\text{COO})\text{SCN}$. Further addition of thiocyanate converts this into $\text{Zn}(\text{NH}_2\text{CH}_2\text{COO})(\text{SCN})_2^-$, lowering the $\text{C}\equiv\text{N}$ stretching frequency to 2100 cm^{-1} .

In the solution containing equimolar quantities of ZnCl_2 , glycine, and sodium thiocyanate, it is possible that, instead of the mixed complex species $\text{Zn}(\text{NH}_2\text{CH}_2\text{COO})\text{SCNCl}^-$ being present, there may exist a mixture of two complex species $\text{Zn}(\text{NH}_2\text{CH}_2\text{COO})_2$ and $\text{Zn}(\text{SCN})_2\text{Cl}_2^{2-}$. If such were the case, the observation that further addition of thiocyanate results in the disappearance of the $\text{Zn}-\text{Cl}$ Raman line would mean that the latter species becomes $\text{Zn}(\text{SCN})_4^{2-}$. This species however, has the $\text{C}\equiv\text{N}$ stretching frequency at 2114 cm^{-1} .¹⁹ However, the observed value of 2100 cm^{-1} in our solutions rules out existence of this tetrathiocyanato species. Furthermore, if the species formed were $\text{Zn}(\text{NH}_2\text{CH}_2\text{COO})(\text{SCN})_2^-$ plus $\text{Zn}(\text{NH}_2\text{CH}_2\text{COO})\text{Cl}_2^-$, the $\text{Zn}-\text{Cl}$ line would be expected at 287 cm^{-1} , as noted earlier, and not at 275 cm^{-1} , as observed. These observations would seem to indi-

cate that there indeed exists the ternary complex species $\text{Zn}(\text{NH}_2\text{CH}_2\text{COO})\text{SCNCl}^-$ in these solutions.

The shifting of the $\text{C}-\text{S}$ stretching frequency of the thiocyanate ion from 747 to 820 cm^{-1} suggests that the thiocyanate is bound to the metal through its nitrogen end.¹⁹ However, a Raman line corresponding to this $\text{Zn}-\text{N}$ stretching vibration was not detected.

Cadmium-Glycine Systems.—Studies with $\text{Cd}(\text{II})$, instead of $\text{Zn}(\text{II})$ in the above experiments, yielded results which were almost identical with those obtained with $\text{Zn}(\text{II})$. A solution of $\text{Cd}(\text{NO}_3)_2$ and glycine at pH 2 gave Raman spectra, with the $\text{C}-\text{C}$ stretching frequency shifted up to 902 cm^{-1} . When chloride ions were present in these solutions, the $\text{Cd}-\text{Cl}$ stretching frequency²⁰ was also observed as a polarized Raman line at 230 cm^{-1} . This value for the $\text{Cd}-\text{Cl}$ stretching frequency, which is quite different from the one for cadmium tetrachloride at 259 cm^{-1} ,²⁰ shows clearly the presence of a mixed complex species in solution, containing both the chloride ion and the monodentate glycine. Fedorov and Balakaeva²¹ have isolated a number of monodentate cadmium-glycine complexes such as $\text{Cd}(\text{GH})_2\text{Br}_2$, etc., where GH refers to a glycine molecule, but they do not specify which end of the glycine is bound to the metal. From our spectra, from the similarity between the $\text{Cd}(\text{II})$ - and the $\text{Zn}(\text{II})$ -glycine spectra, we conclude that in the cadmium complexes also the oxygen atom of the carboxylate group is bound to the metal.

When the pH of these $\text{Cd}(\text{NO}_3)_2$ -glycine solutions is raised to about 5.0, changes take place similar to those for the $\text{Zn}(\text{II})$ -glycine solutions. The $\text{C}-\text{C}$ stretching frequency shifts to around 915 cm^{-1} and new polarized Raman lines appear around 400 cm^{-1} . The spectrum of the ligand at this pH is characteristic of bidentate coordination, and the low-frequency Raman line can be assigned to the $\text{Cd}-\text{N}$ stretching vibration. An equimolar solution of $\text{Cd}(\text{NO}_3)_2$ and glycine at pH 5 shows this line at 415 cm^{-1} , and the solutions containing mole ratios of glycine to $\text{Cd}(\text{II})$ of 2 and 3 show this line at 405 cm^{-1} . In none of the solutions is there appreciable free glycine as shown by the sharpness of the $\text{C}-\text{C}$ stretching frequency at *ca.* 915 cm^{-1} . For these reasons and because of the similarity of the $\text{Cd}(\text{II})$ -glycine system to the $\text{Zn}(\text{II})$ -glycine system, we can conclude that in this case also these complex species exist, containing mole ratios of glycine to $\text{Cd}(\text{II})$ of 1, 2, and 3, respectively.

If CdCl_2 is used in the above solutions in place of the $\text{Cd}(\text{NO}_3)_2$, a new polarized Raman line appears at 230 cm^{-1} for the equimolar CdCl_2 -glycine solutions. This line can be assigned to the $\text{Cd}-\text{Cl}$ stretching vibration. When the ratio of glycine to the metal is increased to 2 and 3, this line disappears. We can conclude that there exists at least one mixed complex species and, by analogy with the similar zinc system, it should be $\text{Cd}(\text{NH}_2\text{CH}_2\text{COO})\text{Cl}_2^{2-}$.

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When potassium thiocyanate is added to a solution containing equimolar $\text{Cd}(\text{NO}_3)_2$ and glycine at pH 5.0, the thiocyanate yields a spectrum characteristic of coordinated SCN^- . At lower thiocyanate concentrations, the $\text{C}\equiv\text{N}$ stretching frequency appears at 2100 cm^{-1} and, as the thiocyanate concentration is increased, this line moves down to 2095 cm^{-1} , indicating, as in the case of the $\text{Zn}(\text{II})$ system, the presence of mixed thiocyanato-glycine complexes with $\text{Cd}(\text{II})$. If thiocyanate is added to an equimolar solution of CdCl_2 and glycine, at pH 5, for small amounts of added thiocyanate, the $\text{Cd}-\text{Cl}$ stretching frequency moves down to 215 cm^{-1} . When more thiocyanate is added, this line disappears completely. The $\text{C}\equiv\text{N}$ stretching frequency in all of these solutions is located at 2095 cm^{-1} . These results are very similar to those obtained for the ZnCl_2 -glycine-thiocyanate system, and accordingly we conclude that the ternary complex $\text{Cd}(\text{NH}_2\text{CH}_2\text{COO})\text{SCNCl}^-$ probably exists in these solutions. The $\text{C}-\text{S}$ stretching frequency of the coordinated thiocyanate is located at 775 cm^{-1} in all of these solutions, indicating bonding of the SCN^- group to the metal through the nitrogen atom.¹⁹

Beryllium Chloride-Glycine System.—Spectra of BeCl_2 -glycine solutions exhibited behavior very different from those of the $\text{Zn}(\text{II})$ - and the $\text{Cd}(\text{II})$ -glycine systems. At pH near 2.0, the Raman spectrum of BeCl_2 -glycine solutions shows the $\text{C}-\text{C}$ stretching frequency around 915 cm^{-1} . The NH_2 stretching frequencies could not be detected, and the $\text{C}-\text{H}$ stretching frequencies for these solutions are at 2975 and 3010 cm^{-1} , indicating that the amino group is protonated. The large shift of the $\text{C}-\text{C}$ stretching frequency indicates strong coordination of the ligand to the metal,

and, because the amino group is protonated, glycine seems to bind only through the oxygen atom of the carboxyl group. The solution containing a mole ratio of glycine to BeCl_2 of 1 shows the $\text{C}-\text{C}$ stretching frequency at 920 cm^{-1} ; the solution containing a mole ratio of glycine to BeCl_2 of 2 shows this line at 915 cm^{-1} . However, when the ratio of glycine to the metal is increased, the line moves down toward 896 cm^{-1} , which corresponds to the free glycine frequency. These results seem to suggest that the $\text{Be}(\text{II})$ coordinates only two glycine molecules. All of these solutions show a weak, broad Raman line at 440 cm^{-1} , which probably arises from a $\text{Be}-\text{O}$ stretching vibration. When the pH of an equimolar solution of glycine is lowered below 1, the complex begins to dissociate, showing a Raman line at 869 cm^{-1} , characteristic of the $\text{C}-\text{C}$ stretching vibration of the $\text{NH}_3^+\text{CH}_2\text{COOH}$ ion, in addition to the line at 920 cm^{-1} .

As the pH of the above solution is increased progressively, the $\text{C}-\text{C}$ stretching frequency shifts down, and, at pH 6.5, it moves down to 896 cm^{-1} . The rest of the glycine spectrum is still characteristic of the protonated amino group, and the entire spectrum resembles very closely the spectrum of the free glycine dipolar ion, $\text{NH}_3^+\text{CH}_2\text{COO}^-$. These changes can only be taken to mean that, as the pH is increased, the $\text{Be}(\text{II})$ ion is hydrolyzed with the consequent dissociation of the glycine from the metal. Thus, at no stage in the pH range between 1.0 and 6.5 does the glycine seem to form a bidentate complex with the $\text{Be}(\text{II})$ ion.

The BeCl_2 -glycine solutions at higher pH show a very weak, broad Raman line at 430 cm^{-1} . Probably this line may be characteristic of some hydrolyzed $\text{Be}(\text{II})$ ion.

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Product Competition Ratios in Substitution Reactions of Pentaamminecobalt (III) Complexes

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Studies of the competition between water and other species as entering groups in the replacement of L from $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{L}$ have been extended. The oxygen isotopic fractionation effect has been found to be the same within experimental error (± 0.001) for HgCl^+ , HgBr^+ , N_3^- , NO^+ , Cl^- , Br^- , and NO_2^- as leaving groups. Trimethyl phosphate has been investigated as a leaving group. It is found that the competition ratios are different from those reported by Haim and Taube for two other systems involving neutral leaving groups.

Introduction

The question as to whether an intermediate of reduced coordination number is formed in substitution reactions can in principle be settled by investigating the relative reactivity of the intermediate to a variety of incoming groups. Using this approach and comparing the results of chemical competition studies for

the nitrous acid assisted removal of azide ion from $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ on the one hand with those derivable from measurements of the rates of anation of $\text{Co}(\text{NH}_3)_5\text{-H}_2\text{O}^{3+}$, Haim and Taube¹ concluded that a common intermediate is formed in the two kinds of reactions. By extending this kind of measurement to reactions in

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