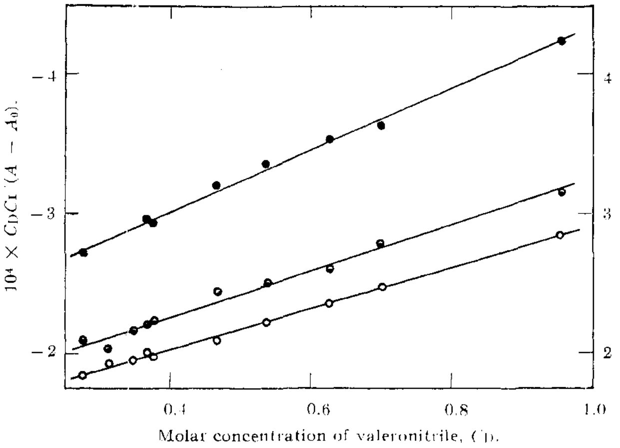

Figure 1.—Plots of $C_DC_I/(A - A_0)$ vs. C_D at 25° for 560 (●), 540 (◒), and 460 (○) mμ. The left-hand ordinate is for 560 and 540 mμ; the right-hand ordinate is for 460 mμ.

Table II

Data at 237.5 mμ for Valeronitrile–Iodine in Heptane at 25°

C_D	10^3C_I	$A - A_0$ (exptl)	$A - A_0$ (calcd)
0.1200	1.628	−0.302	−0.300
0.1936	1.627	−0.453	−0.455
0.2495	1.623	−0.556	−0.559
0.3053	1.625	−0.656	−0.654
0.3470	1.630	−0.727	−0.724
0.4078	1.640	−0.818	−0.819

$K_c = 0.99$

for 560 and 460 mμ, for example, is 6 and 13, respectively, while at 237.5 mμ, a sharpness of 25.5 is obtained. Although the sharpness of fit in the visible region is lower than hoped for, the consistency of the results at the different wavelengths in this region together with the agreement with the result found at 237.5 mμ substantiates the reliability of the values of K_c listed in Table III. Plots similar to Figure 1 were drawn for the other temperatures and wavelengths.

Table III

Values of the Formation Constant, K_c, at Different Temperatures

Temp, °C	K_c,[a] l. mole^{-1}
25.0	1.02 ± 0.03
35.0	0.94 ± 0.08
45.0	0.80 ± 0.10
50.0	0.71 ± 0.08
55.0	0.65 ± 0.02

[a] Each K_c listed is the average of the K_c values at the different wavelengths.

From the data in Table III, a $\Delta H°$ value of -3.0 ± 0.3 kcal/mole and a $\Delta S°$ value of -9.8 ± 0.8 eu were obtained. The uncertainties are the standard deviations estimated by the least-squares method. The value of 1.02 obtained for K_c at 25° is considerably larger than the value of 0.46 predicted for iodine complexes from the equation of Person, Golton, and Popov.[3] This difference is considered to be well outside the range of experimental indetermination and indicates that simple inductive effect considerations, as reflected by the Taft σ^* values, while effective in predicting the variation in K_c with halogen substitution, are of quite limited use when a different kind of substitution is involved. It should be pointed out that any contribution due to steric effects would be expected to make the value of K_c smaller than that predicted from σ^* rather than larger as observed.

Another correlation which is often made in charge-transfer complexes involves a linear variation of $\Delta H°$ with $\Delta S°$. Person, Golton, and Popov[3] have found that for the substituted acetonitriles and halogens the equation $\Delta S° = 1.85\Delta H° - 5.6$ can be written. It is interesting to note that the values of $\Delta H°$ and $\Delta S°$ found by us for the valeronitrile–iodine system fit this equation quite well.

The equilibrium formation constants have been measured for only three aliphatic nitriles with iodine (acetonitrile,[3,9] propionitrile,[10] and chloroacetonitrile[3]). The value for acetonitrile–iodine has been determined with good agreement by two different investigators and can be regarded with some confidence. In the case of chloroacetonitrile, however, the high nitrile concentration (6 *M*) used to obtain measurable amounts of complex formation could cause an appreciable change in the dielectric constant of the system and affect the value of K_c observed. As yet there are not sufficient data available for the iodine–nitrile systems to permit more than semiquantitative evaluation of the influence of substituent groups on the value of K_c, but it seems that other than simple inductive and steric arguments must be considered.

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The Binding of Mercury(II) by Glycine. A Raman Spectral Study

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Raman spectroscopy is a convenient technique for studying complexes of d^{10} ions, which do not possess spectral or magnetic properties that allow their characterization by other methods. Furthermore, the low Raman intensities of water bands permit study of these complexes in aqueous solution, free from the strong intermolecular interactions which influence infrared measurements of the crystalline state.

As a part of a general investigation of the binding sites and structures of amino acid complexes of zinc(II), cadmium(II), and mercury(II) in aqueous solution we have recorded the Raman spectra of the glycine complexes. This study was dictated because glycine is the protypal amino acid possessing the ligating α-amino and α-carboxyl groups. The spectra of the glycine complexes of Zn(II) and Cd(II) have recently been reported,[1] and our investigations are in agreement with those findings. Krishnan and Plane did not record the Raman spectrum of the mercury(II)–glycine system, however. This system is the subject of the present note, for when compared with those of Zn(II) and Cd(II), several important differences are revealed.

Experimental Section

All chemicals used were reagent grade. The glycine (Eastman Organic Chemicals, Rochester, N. Y.; ammonia-free, mp 245°) was recrystallized, treated with activated charcoal, and filtered in order to remove fluorescent impurities. The mercury(II)–glycine solutions were approximately 3.0 *M* in glycine and 1.5 *M* in mercury(II) nitrate. After 12–24 hr, noticeable decomposition of the glycine occurred with concurrent reduction of the Hg(II) to mercury metal.[2] Only fresh solutions prepared less than 1 hr before recording the spectrum were used in these studies, and the effects of decomposition were so avoided.

A Cary Model 81 Raman spectrophotometer was used to record the spectra with the 4358-A mercury line as the exciting frequency. This line was isolated with a Du Pont Rhodamine 5GDN-Extra filter solution and an Eastman Kodak Wratten 2a single-sheet filter. The wavenumber scale was calibrated in the region 0–4000 cm^{-1} using known frequencies of carbon tetrachloride, methyl chloride, dimethyl sulfide, and certain mercury lines. Recorded relative intensities represent relative planimetered areas of Raman bands, and these are accurate to approximately 10%. Estimated error in observed frequencies is ±4 cm^{-1} except in the 230-, 575-, and 1200-cm^{-1} bands for which the frequencies are accurate to ±10 cm^{-1}.

Results and Discussion

The lines observed in the Raman spectrum of the mercury(II)–glycine system are presented in Table I along with those in the spectra of the fully protonated glycine and acidic zinc(II)–glycine solutions. It was possible to study the mercury(II)–glycine system only at pH <2.0 because further addition of base resulted in formation of a precipitate, presumably a mercury–hydroxo species. In contrast to its behavior in the zinc and cadmium systems, glycine is bidentately bound to Hg(II) even under these acidic conditions. Since mercury(II) nitrate was used in preparation of the complex, the spectrum contains certain lines which are attributable to free NO_3^-. No frequencies corresponding to bound nitrate were observed.[3] Some of the glycine lines are approximately coincident with those of the free nitrate ion, and accurate resolution was not possible in these cases. The assignments adopted for lines above 490 cm^{-1} are those made from Urey–Bradley force field analyses of glycine[4] and its 1:1 metal complexes.[5] Detailed arguments for assignments of frequencies below 490 cm^{-1} follow.

TABLE I

RAMAN SPECTRA OF GLYCINE, ZINC(II)–GLYCINE, AND MERCURY(II)–GLYCINE SOLUTIONS (CM^{-1})[a,b]

Glycine[c] pH 1.5	Zn(II)–gly[d] pH 2	Hg(II)–gly pH 1.5	Assignment
3011 s	3015 s	3014 (0.52)	CH_2 str
2975 vs	2975 vs	2969 (3.0)	CH_2 str
1744 s	...	1728 (0.74)	C=O str (free gly)
1644 vs	...	1644 (1.02)	CO_2^- antisym str (free gly)
...	1610 m	1589 (1.13)	CO_2^- antisym str (bound gly)
1433 m	1440 s, sh	1441 (1.64)	CH_2 scissor
...	1418 vs	1403 (1.50)	CO_2^- sym str (also, $\nu_3(E')$ NO_3^- in Hg(II)–gly)
...	1335 s	1350 (1.21)	CH_2 wag (bound gly)
1308 s	...	1307 (0.91)	CH_2 wag (free gly)
...	1175 vw	1200 (0.55)	CH_2 twist
1123 w	1110 m, b	1136 (0.23)	NH_2 twist, NH_3^+ rock
1042 m	1030 m	1046 vs (∼5.0)	CN str, $\nu_1(A_1')NO_3^-$
...	902 vs	912 (1.35)	CC str (bound gly)
869 s	...	869 (0.33)	CC str (free gly)
...	...	717 (0.70)	NO_3^- $\nu_4(E')$
644 w	670 vw	...	CO_2^- scissor
...	580 vw	575 (0.88)	CO_2^- wag
494 m	500 s	498 (0.77)	CO_2^- rock, NH_3^+ torsion
...	...	464 (1.00)	MN str
...	395 w	385 (0.39)	MO str
...	...	325 (0.42)	CCN bend (bound gly)
...	...	298 (0.28)	CCN bend (free gly)

[a] s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder. [b] Numbers in parentheses represent intensities relative to that of the line assigned to the metal–nitrogen stretch. [c] S. A. S. Ghazanfar, D. V. Myers, and J. T. Edsall, *J. Am. Chem. Soc.*, **86**, 3439 (1964). [d] See ref 1.

The moderately strong polarized line at 464 cm^{-1} is assigned to the metal–nitrogen stretch. This assignment is congruent with that made for the mono- and bisglycine–zinc(II) complexes at 445 and 430 cm^{-1}, respectively, and for the corresponding frequencies in the bis complexes of *trans*-Pt(II), *cis*-Pt(II), *trans*-Pd(II), *trans*-Cu(II), *cis*-Cu(II), and *trans*-Ni(II) (549, 554, 550, 439, 460, and 439 cm^{-1}, respectively).[5] The metal–nitrogen stretching frequency of the mercury(II)–glycine complex appears at 54 cm^{-1} higher than that of the tetraamminemercury(II) complex (410 cm^{-1}),[6] consistent with the formation of a stronger metal–ligand bond in the chelate. Although Zn(II) and Cd(II) do not bind to the nitrogen atom of the zwitterionic glycine at pH <3, the mercury(II)–nitrogen bond is apparently strong enough to compete favorably with the amino protonation process under quite acidic conditions. Moreover, the appearance of the Hg(II)–N stretch at a higher frequency than the corresponding modes in the zinc(II)- and cadmium(II)-glycine systems (observed at 445 and 415 cm^{-1}, respectively[1])

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(2) This reaction is under investigation.

(3) R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 769 (1964).

(4) S. Suzuki, T. Shimanouchi, and M. Tsuboi, *Spectrochim. Acta*, **19**, 1195 (1963).

(5) R. A. Condrate and K. Nakamoto, *J. Chem. Phys.*, **42**, 2590 (1965).

(6) R. A. Plane, "Proceedings of the 8th International Conference on Coordination Chemistry," Vienna, 1964, p 17.

affirms a tighter metal–amino bond in the former complex.

The extremely weak band at 385 cm^{-1} is attributed to a metal–oxygen stretching mode. The metal–oxygen stretch in the mercury(II)–aquo complex has been detected at 380 cm^{-1}.[7] The possible assignment of this band to the glycine complex would be consistent with infrared studies on other metal–glycine systems.[5] As no other line attributable to a metal–oxygen frequency is observed, it is impossible to distinguish whether this band is due to a mercury–aquo or mercury–glycino complex or both. The formation of a bidentate complex with binding by the carboxylate group is indicated by the appearance of a strong line due to a carbon–carbon stretch in the chelate at 912 cm^{-1} and by the appearance of a chelate ring deformation mode at 230 cm^{-1}. Condrate and Nakamoto's analysis[5] indicates that such a ring mode should be observed at *ca.* 215 cm^{-1}, but this vibration remained undetected in their measurements which were extended to only 250 cm^{-1}. The line at 298 cm^{-1} is assigned to the CCN bending of the free glycine in agreement with the calculated frequency range of 297–308 cm^{-1}.[4] This bending frequency would be expected to increase in energy upon chelation, and the line at 325 cm^{-1} may be ascribed to the analogous vibration in the metal complex. Unfortunately, with the exception of the 464-cm^{-1} line, the weak intensities of the low-frequency bands precluded polarization studies.

Whereas chelation may be confirmed by the appearance of new bands at low energies, complementary evidence from frequency shifts is obtained in the high-frequency region. Although some glycine remains in the free cationic form at pH 1.5, deprotonation and binding of the carboxylate group to the Hg(II) is indicated by the shift in the C–C stretch from 869 to 912 cm^{-1}. The shifts observed in the CO_2^- antisymmetric stretching frequency are of particular interest. This mode appears in the Raman spectra at 1611, 1615, and 1644 cm^{-1} in the anionic, zwitterionic, and cationic forms of free glycine.[8] The shift upon protonation of the amino group has been attributed to an inductive effect accompanying increase in positive charge on the nitrogen atom.[9] For the amino acids cysteine[10] and alanine[11] it has been argued that the increase in this frequency upon complexation to a variety of metals can be used as a measure of the relative enthalpies of formation of the metal–nitrogen bond. This empirical correlation depends on a small shift in the antisymmetric carboxylate frequency upon complexation of the carboxylate group and a substantial frequency shift of this mode upon protonation of the nitrogen of the anion to form the zwitterion.[10,11] For glycine there is a relatively large increase in the antisymmetric carboxylate frequency on protonation of the carboxylate group ($\Delta\nu$ = 29 cm^{-1}), while the shift in this frequency upon forming the zwitterion is only 4 cm^{-1}.[8] Since it is apparent that neither of the conditions on which the enthalpy–carboxylate frequency correlation was based in the alanine and cysteine systems holds for the glycine case, it is not surprising that one observes a decrease in the frequency of the antisymmetric carboxylate stretch in the zinc–, cadmium–, and mercury–glycine complexes (recorded at 1610, 1600, and 1589 cm^{-1}, respectively). An examination of the potential energy distributions for glycine[4] and its complexes[5] reveals that other vibrations contribute significantly to the observed frequency at *ca.* 1600 cm^{-1}, and this may not be ignored in eliciting secondary information from frequency shifts upon glycine coordination.

For the glycine complexes an alternate criterion for the strength of a chelate bond is the frequency attributable principally to the metal–ligand vibration. Although other normal modes do affect this frequency, the main contributions arise from low-frequency motions that appear only on complex formation or modes directly involving the ligand atom participating in the complex bond of interest. For the glycine complexes this criterion would support the ordering of metal–nitrogen bond strengths for divalent metals: Pt(II) (554, 549 cm^{-1}) $\sim$ Pd(II) (550 cm^{-1}) $>$ Hg(II) (464 cm^{-1}) $\sim$ Cu(II) (460, 439 cm^{-1}) $>$ Ni(II) (439 cm^{-1}) $>$ Zn(II) (430 cm^{-1}) $>$ Cd(II) (415 cm^{-1}), in complete agreement with the stability of these complexes.[12]

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Infrared Spectra in Polarized Light of $Na_2[Fe(NO)(CN)_5]\cdot 2H_2O$

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The assignment of the M–N stretching and M–NO rocking frequencies of nitrosyl complexes has been made so far only for the compound $[Co(NO)(CO)_3]$.[1] By isotopic substitution with ^{15}N it has been possible to assign the absorption bands at 594 and 565 cm^{-1} to the Co–N stretching and Co–NO rocking frequencies, respectively.

The infrared spectrum of nitrosyl complexes of the type $[M(NO)(CN)_5]^{n-}$ usually exhibits two absorption bands in the 670–600-cm^{-1} region, while the complexes of the type $[M(NO)X_5]^{n-}$ exhibit two bands in the 620–530-cm^{-1} region.[2,3] The assignment of these absorption bands is till controversial. Some authors

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