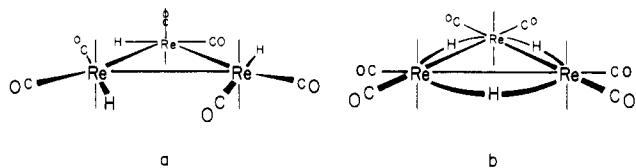


proceeding from the repeating unit related to *cis*-HLRe(CO)₄ such as structure Ia (in which the axial



I

carbonyl groups have been omitted for purposes of clarity). This structure is favored for a number of reasons. For one, the carbonyl groups are less crowded; this can be seen on models constructed from atoms whose dimensions were taken similar to those in Os₃(CO)₁₂.¹¹ In addition the *cis* six-coordinated species HLRe(CO)₄ is probably the more likely precursor to the formation of trimer, since reactions of derivatives XM(CO)₃ are observed to give predominantly *cis* substitution.²⁵

We would expect, however, that a trimer such as Ia would give rise to more than four principal absorptions in the region 2150-1900 cm.⁻¹. Four carbonyl and one metal-hydrogen stretching absorptions are expected in this region, arising from each of the repeating units and therefore at least as many could be expected in the trimer as a whole. However, the position of the hydrogen atoms in structure Ia suggests a remedy which would be in keeping with the lack of a metal-hydrogen stretch-

(25) F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 79 (1961).

ing frequency in the high energy region. A small displacement of each hydrogen toward the adjacent metal, as in Ib (in which the axial carbonyl groups have been omitted for purposes of clarity) would result in hydrogen-bridged metal-metal bonds and an increase in the coordination number of the metal to eight, neither of which possibilities are excluded by any principles in theory that we know. In this model the correct number of carbonyl bands is predicted either from the symmetry of the repeating unit, C_{2v}, or of the trimer as a whole, D_{3h}.²⁴ Also, it would explain the lack of a distinct metal-hydrogen stretching frequency in the infrared in the region where these have been observed to occur, which we failed to observe for the present derivative. Such an arrangement of bridging hydrogen atoms would probably be reflected by some unusual length for the Re-Re bond. Of course, the hydrogen atoms would be located only through a neutron diffraction study which would have to follow a single crystal X-ray study.

Acknowledgments.—We are greatly indebted to Professor L. F. Dahl of the University of Wisconsin for valuable discussions concerning the structure of the trimer, and to several other colleagues, as mentioned in the text, for their assistance in the magnetic susceptibility measurements and X-ray powder patterns. Our thanks are also extended to Mr. Robert Marshall of these laboratories for assistance in the construction of the models referred to in the discussion, and to Mr. Robert Harrill for assistance with deuteration experiments with HRe(CO)₅.

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Metal Ion Catalysis in Transamination. II. Pyruvate-Glycinate Equilibrium Systems with Some Divalent Metal Ions^{1,2}

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The complexes of MPG, MPG₂⁻, MP₂G₂⁻² (P⁻ = pyruvate, G⁻ = glycinate, and M = Mn(II), Ni(II), or Zn(II), and CaPG have been found to form in solution and their stabilities have been determined. The "mixed" complexes containing both P⁻ and G⁻ have substantially greater stabilities than the analogous simple complexes. With the different metal ions the PG⁻² combination is shown to behave similarly to the tridentate ligand, iminodiacetate. The intrinsic stabilities of the MP₂G₂⁻² species are greater than those of the MPG complexes, a property which seems to be characteristic of coordination to unsaturated nitrogen. Spectral data give further evidence that this is so. These results support the recent conclusions of a p.m.r. study that the complexed ligands are condensed as a Schiff base. An evaluation of the temperature dependences of the equilibria qualitatively shows that entropy contributions are important in stabilizing the Ni(II)- and Zn(II)-PG⁻² systems, but appear to be less important with Mn(II).

Transamination between oxo and amino acids is one of the enzymatic reactions that can be duplicated in model systems containing metal ions.³⁻⁸ The reactive species appear to be "mixed" complexes in which it is thought the ligands are condensed as Schiff bases. A complicating factor in the interpretation of the results

is the extensive dissociation of most Schiff bases in aqueous solutions.

The application to these systems of the Bjerrum "pH-titration" technique, which is capable of providing much information, and the use of a high-speed computer to analyze the data has recently been proposed.⁹

In a study^{1,9} of the Ni(II)-pyruvate-glycinate system, mixed complexes of unusually high stabilities were found. In order to discover more of the properties of these mixed complexes, the earlier work has been extended to include Ca(II), Mn(II), and Zn(II). The behavior at temperatures other than 25° was examined.

(1) Part I in this series: D. L. Leussing, *Talanta*, **11**, 189 (1964).

(2) Supported by a grant from the National Science Foundation.

(3) D. E. Metzler and E. E. Snell, *J. Am. Chem. Soc.*, **74**, 979 (1952).

(4) L. Davis, F. Roddy, and D. E. Metzler, *ibid.*, **83**, 127 (1961).

(5) H. N. Christensen, *ibid.*, **80**, 2305 (1958).

(6) H. Mix, *Z. physiol. chem.*, **515**, 1 (1959).

(7) L. J. Nunez and G. L. Eichhorn, *J. Am. Chem. Soc.*, **84**, 901 (1962).

(8) B. E. C. Banks, A. A. Diamantis, and C. A. Vernon, *J. Chem. Soc.*, 4235 (1961).

(9) D. L. Leussing, *J. Am. Chem. Soc.*, **85**, 231 (1963).

TABLE I
THE LOGARITHMS OF THE FORMATION CONSTANTS

$$\beta_{MP_2G_2} = \frac{(MP_2G_2)}{(M^{+2})(P^-)^2(G^-)^2}$$

Cumulative constant for	M							
	Ca 25°	Mn		Ni		Zn		
	25°	10°	25°	10°	25°	10°	25°	
MP	0.8 ^a	1.20	1.26	1.40	1.15	0.90	1.28	
MG	1.4 ^b	2.66	2.60	5.73	5.66	4.96	4.88	
MG ₂	...	4.71	4.58	10.80	10.51	9.24	9.01	
MG ₃	...	6.0	5.7	14.4	14.0	11.9	11.0	
MPG	(3.9)	5.51 ± 0.02	5.36 ± 0.02	8.19 ± 0.07	8.09 ± 0.02	7.61 ± 0.02	7.53 ± 0.02	
MPG ₂	...	7.7 ± 0.6	6.9 ± 0.03	13.57 ± 0.09	13.00 ± 0.04	11.54 ± 0.25	12.0 ± 0.1	
MP ₂ G ₂	...	10.25 ± 0.03	9.79 ± 0.03	15.76 ± 0.05	15.29 ± 0.02	14.54 ± 0.02	14.25 ± 0.02	
pK _{1a} for glycine:		2.78 (10°), 2.46 (25°), 2.23 (40°)						
pK _{2a} for glycine:		10.10 (10°), 9.70 (25°), 9.28 (40°)						
pK _a for pyruvic acid:		2.39 (10°), 2.39 (25°), 2.22 (40°)						

^a J. Schubert and A. Lindenbaum, quoted by J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," The Chemical Society, London, 1957, Part I. ^b C. W. Davies, see footnote a.

Spectral data were obtained for the mixed Ni(II) complexes and are compared with those of simpler Ni(II) species. Spectra in the ultraviolet region were also obtained.

Experimental

Pyruvic acid, Matheson Coleman and Bell, was either twice vacuum distilled or vacuum distilled and twice recrystallized by partial freezing. The latter method was more successful in removing the last small amount of water. The purified material was stored at temperatures below its freezing point.

Glycine, from the same source, was recrystallized from 50:50 ethanol-water mixtures and dried *in vacuo*.

Stock solutions of the metal chlorides were standardized by titration with EDTA.¹⁰

To determine the stabilities of the mixed complexes in a typical experiment, accurately measured volumes of solutions of the metal chloride, pyruvic acid, and potassium chloride were mixed and brought to a final volume with water. This solution was then titrated under nitrogen with a glycine solution which had been neutralized with NaOH. The pH was measured after each addition of titrant. At 25°, the initial solution compositions were of the order of 0.050 M with CaCl₂ and 0.020 M with MnCl₂ and ZnCl₂ over a series of pyruvic acid concentrations of 0.05, 0.10, and 0.15 M. In the last two runs, sufficient NaOH was added to reduce the concentration of unneutralized pyruvic acid to 0.050 M. The concentration of potassium chloride was adjusted in each run so that the initial ionic strength was maintained at 0.65 M. Similar experiments were run at 10 and 40°, but with Mn(II) and Zn(II) the concentration of MCl₂ was 0.050 M to accentuate the formation of MPG₂⁻. The previous Ni(II) study^{1,9} at 25°, conducted using 0.020 and 0.050 M NiCl₂ levels, indicates that no appreciable effect results from this slight change in conditions. Over the course of the titrations (see Fig. 1), the ionic strengths are calculated to decrease by about 0.04 unit.

The reaction rates at 25° were found to be moderate. The order of 10 min. was required for a constant pH value to be attained after each addition of titrant. At 10° the equilibration rates were slower, but even so, direct titrations of the Mn(II) and Zn(II) solutions were still feasible. The Ni(II) reactions, however, were so slow (24 hr. for equilibration) that batch-wise experiments were run; each point on the titration curve represents a separately prepared solution.

At 40°, the complex formation rates were found to be faster, but a secondary reaction, which was manifested by a slow increase in the pH, was found to set in. This secondary reaction was especially noticeable with Ni(II). The pH rise was found to result from the slow disappearance of pyruvate. In a separate set of experiments, solutions were made up to contain initially

0.050 M MCl₂, 0.050 M glycine, 0.075 M sodium glycinate, and 0.010 M sodium pyruvate. The pyruvate concentration was monitored as a function of time by periodically removing aliquots, decomposing the complexes by quenching in 1.0 M HCl, diluting 10-fold, and determining the magnitude of the polarographic diffusion current of the pyruvic acid. With Ni(II) at 40°, a 9% decrease in the pyruvate concentration was noted after 2 hr. Zn(II) under the same conditions gave a 5% decrease. At 25° Ni(II) produces only a 2% decrease in 2 hr. Experiments in a closed system showed no evidence of CO₂ evolution with Ni(II) after 7 hr. at 40°. Apparently, the pyruvate consumption results from the metal ion catalyzed dimerization.^{11a} The stabilities of the simple metal ion glycinate and pyruvate complexes were determined under identical conditions. The constants for the overlapping glycinate complexes were obtained graphically.^{11b} Excellent linear plots were obtained, but most likely the accuracy in the first two constants is no better than ± 0.02 log unit owing to the limitations of the pH measurements.

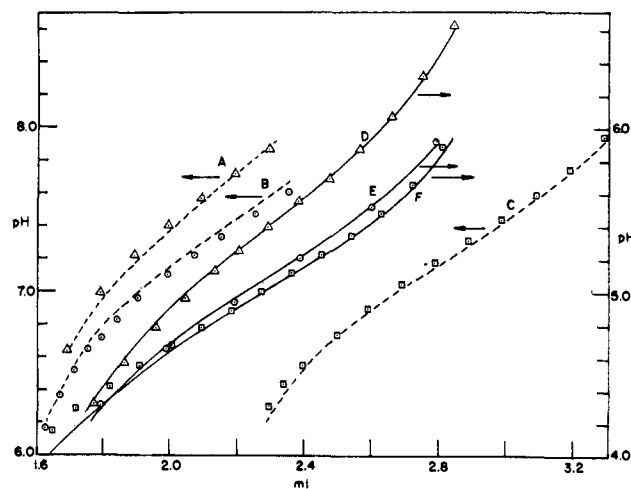


Fig. 1.—Titration curves of Mn(II) and Zn(II) pyruvate solutions with sodium glycinate: initial volume, 25 ml.; concentration of NaG, 0.803 M. — — —, Mn(II): A, 0.0500 M HP, 0.0204 M Mn(II); B, 0.0505 M HP, 0.0495 M NaP, 0.0204 M Mn(II); C, 0.0689 M HP, 0.0781 M NaP, 0.0200 M Mn(II). — — —, Zn(II): D, 0.0505 M HP, 0.0201 M Zn(II); E, 0.0554 M HP, 0.0456 M NaP, 0.0201 M Zn(II); F, 0.0534 M HP, 0.0922 M NaP, 0.01934 M Zn(II) (26 ml.).

The combined effects of the high acidity of pyruvic acid and the

(10) G. Schwarzenbach, "Complexometric Titrations," translated and revised by H. Irving, Interscience Publishers, New York, N. Y., 1957.

(11) (a) D. L. Leussing and C. K. Stanfield, *J. Am. Chem. Soc.*, **86**, 2805 (1964); (b) E. L. King and P. K. Gallagher, *J. Phys. Chem.*, **63**, 1073 (1959).

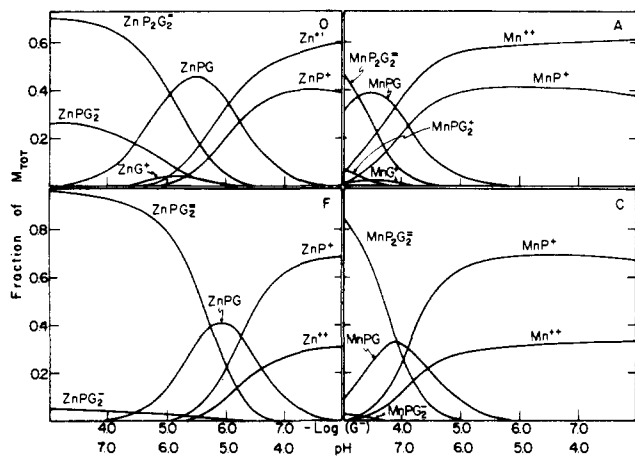


Fig. 2.—Distribution of metal ion in some of the titrations of Fig. 1.

low stabilities of the pyruvate complexes cause these species to lie on the borderline of those which can be determined by the pH technique. It is necessary to correct for the free hydrogen ion concentration in solution, and the data for this were obtained by titrating KCl blanks with standard HCl. Evidence for only mono complexes was obtained. The uncertainties in the constants are of the order of 10–20%.

The results are given in Table I where the values of the over-all constants for the reactions $M^{+2} + pP^- + gG^- \rightleftharpoons M_pPG_g$ are presented. The experimentally observed curves for the Mn(II) and Zn(II) systems are shown in Fig. 1. The solid and dashed lines are drawn through the theoretical points calculated using the constants reported in Table I. The theoretical distribution curves for the titrations of Fig. 1 are presented in Fig. 2. The constant for ZnP^+ is seen to be larger at 25° than at 10° by an amount well outside of what is thought to be the experimental error. Endothermic heats are not uncommon in reactions where electrostatic interactions predominate. The effect results from the decrease in the dielectric constant of water with increasing temperature.¹² Recent n.m.r. studies^{11a} have shown that ZnP^+ is not a single species but consists of a mixture of keto and hydrated, *gem*-diol, forms; thus, a simple explanation of the effect will not suffice.

Supporting evidence that the heat of formation of ZnP^+ is indeed endothermic was obtained by varying the constant for ZnP^+ as well as those for $ZnPG$, $ZnPG_2^-$, and $ZnPG_2^{2-}$ in the Pitmap program described below. These independently determined values for ZnP^+ were also found to be appreciably lower at 10° than at 25°. The experimentally determined values for ZnP^+ were used to obtain the final results given in Table I.¹³

A Radiometer "TTTT" titrator functioning as a pH meter with a scale expander was used to determine the pH. The electrodes were standardized at each temperature against National Bureau of Standards potassium hydrogen tartrate, phosphate, and borate buffers.

Absorption spectra were obtained using a Cary 14 spectrophotometer.

Computer Program.—A detailed numerical study of the Ni(II)–pyruvate–glycinate system was previously made.¹ Theoretical titration curves using assumed sets of constants for the mixed species were computed and these were compared with the observed curves. To assure convergence of each computation on the correct root, the use of the Newton–Raphson refinement was restricted to the evaluation of only one unknown (the pyruvate concentration), and this was performed only under carefully controlled conditions. This procedure had the disadvantage that an interpolation was required in order to compare observed and theoretical pH values at each point.

Since it was found that only one (the correct) root existed in the

region of positive concentrations for all species, the program was revised so that for each observed volume of titrant a theoretical value of pH was computed, thus avoiding the interpolation. This modification requires the use of the Newton–Raphson method to obtain simultaneously the values of the two unknowns, the glycinate and pyruvate concentrations. Tests are made at various points in the computation and if negative concentrations are found, the initial estimates of the unknowns are systematically varied over a power of ten until some combination of initial values causes convergence on positive roots. Rerunning the earlier Ni(II) data showed that the revised program gave results identical with the earlier procedure within the chosen accuracy.

To find the "best" set of constants, a "Pitmap" technique¹⁴ was used to find the square of the minimum sum of the residuals, $\sum_i (\text{pH}_{\text{theor},i} - \text{pH}_{\text{obsd},i})^2$. Estimated values of the constants to be

refined (up to four) were read into the computer along with the titration data. These constants were systematically varied to obtain the coefficients of the generalized paraboloid which is assumed to describe the residual surface in the region of the minimum, $U = C_{00} + 2C_{01}x_1 + C_{11}x_1^2 + 2C_{02}x_2 + C_{22}x_2^2 + 2C_{03}x_3 + C_{33}x_3^2 + 2C_{04}x_4 + C_{44}x_4^2 + 2C_{12}x_1x_2 + 2C_{13}x_1x_3 + 2C_{14}x_1x_4 + 2C_{23}x_2x_3 + 2C_{24}x_2x_4 + 2C_{34}x_3x_4$, where U is the sum of the square of the residuals and $x_1, x_2, x_3,$ and x_4 are the displacements in the constants being refined. To avoid convergence to a maximum in regions where the surface shows negative curvature, the equation $\partial U / \partial x_i = 0$ ($i = 1, 2, 3, 4$) was not solved if the value of U for a particular combination of x_i was found to be less than the value of C_{00} (*i.e.*, the value of U which is obtained when the displacements are zero for the particular set). The origin was shifted to this lower combination or to the lowest if more than one combination gave a result less than C_{00} , and the process was repeated. Only when no U was found to be smaller than C_{00} was the minimum of the assumed paraboloid computed. If it were thought to be necessary, the region of the minimum was then rescanned using a finer network of constants.

This technique of locating the best fit was highly successful and, when moderately good estimates of the constants were used, proved to be faster than the search method originally proposed.¹

From the shape of the residuals square surface, the standard deviations of the points and constants were calculated.¹⁴

Results and Discussion

In Table I it is seen that the results at 10 and 25° are highly consistent. Except for Ca(II), which was not extensively investigated, three mixed species, MPG , MPG_2^- , and $MP_2G_2^{2-}$, have been found for each metal ion. Figure 2 shows that the first and last of these predominate over the intermediate. While the formation constant of $NiPG_2^-$ has been found with sufficient precision to establish its actual existence,¹⁵ the constants for $MnPG_2^-$ and $ZnPG_2^-$ are not so precise. Since approximately the same values of the constants for these intermediates are found at 10 and 25°, it seems likely that their presence is real rather than a manifestation of experimental error.

As was pointed out earlier,⁹ the prior coordination of one of the components of the mixed complex to the metal ion greatly enhances the coordination of the other relative to its coordination to the aquo metal ion. The magnitude of this effect can be readily seen in the values of the ligand enhancement factors for the formation of MPG given in Table II. The ligand enhancement factor (LEF) is calculated from the equation $LEF = \log \beta_{MPG} - \log \beta_{MP} - \log \beta_{MG}$ and is a quantitative measure of the relative increase in the stepwise constant for the binding of one ligand to a complex where the other is already coordinated compared to the constant for the binding to the simple metal ion.

(14) L. G. Sillén, *Acta Chem. Scand.*, **16**, 195 (1962); N. Ingri and L. G. Sillén, *ibid.*, **16**, 173 (1962).

(15) The constant for $NiPG_2^-$ obtained using a least-squares fit is more in line with the value expected for little interaction between the second glycinate and the PG^{2-} moiety, contrary to the conclusions reported in ref. 9 where single data points had been used in the calculations.

(12) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc., New York, N. Y., 1953.

(13) Correcting for the formation of chloro complexes raises the value for the Zn(II) species given in Table I by about 0.1 log unit using the results of Sillén quoted in "Stability Constants," Part 2 (see footnote a, Table I). S. A. Shchukarev, *et al.*, quoted in this same source, report that the heat of formation of $ZnCl^+$ is 0 kcal./mole.

TABLE II

Temp., °C.	LIGAND ENHANCEMENT FACTORS			
	LEF ^a = log β _{MFG} - log β _{MP} - log β _{MG}			
	Ca(II)	Mn(II)	Ni(II)	Zn(II)
10	...	1.6	1.1	1.7
25	(1.7)	1.5	1.3	1.3

^a This is also the pK for the equilibrium $MP + MG \rightleftharpoons MPG + M$.

TABLE III

Stepwise constants	INTRINSIC CONSTANTS ^a															
	Ca				Mn				Ni				Zn			
	Gly ⁻	IDA ⁻²	PG ⁻²	phen ^b	Gly ⁻	IDA ⁻²	PG ⁻²	phen ^b	Gly ⁻	IDA ⁻²	PG ⁻²	phen ^b	Gly ⁻	IDA ⁻²	PG ⁻²	phen ^b
Log K ₁	0.0	2.0	2.5	...	1.2	...	3.6	2.6	4.3	6.9	6.3	7.2	3.5	5.6	5.7	5.0
Log K ₂	1.3	...	4.0	2.8	4.2	6.1	6.8	7.5	3.5	4.9	6.3	4.95
Log K ₃	(1.4)	3.3	3.3	7.9	2.3	5.3

^a The statistical corrections were made by assuming octahedral configurations and considering the symmetry numbers of the reactants and products: see S. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958). ^b Values recommended by H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5222 (1962).

Two interesting facts emerge from a consideration of the data in Table II. First, in all cases, the LEF values show an increase of over 10-fold in the stepwise constant for the formation of the mixed complex. Second, the effect with Mn(II) (and possibly with Ca(II)) is larger than with either Ni(II) or Zn(II). This is surprising since complexing effects with Mn(II) are usually smaller than those observed with these other two ions.

The enhancements indicate that large ligand-ligand interactions exist within the complexes. Recent n.m.r. studies^{11a} have verified this conclusion and have demonstrated that the coordinated ligands are condensed both as the Schiff base and as another form, probably the hydrated carbinolamine. The former predominates about 2:1.

The constant for the reaction $P^- + G^- \rightleftharpoons PG^{-2}$ has a value of 2.5.^{1,16} Using this value and the data in Table I, it is possible to calculate the constants for the stepwise reactions, $M^{+2} + PG^{-2} \rightleftharpoons MPG$ and $MPG + PG^{-2} \rightleftharpoons M(PG)_2^{-2}$. These stepwise constants are given in Table III along with those reported for the analogous saturated tridentate ligand iminodiacetate (IDA⁻²) and the bidentate ligands 1,10-phenanthroline (phen) and glycinate. To facilitate the comparisons between bi- and tridentate ligands, the values in Table III have been corrected for statistical effects.

Comparing the 1:1 complexes, it is readily seen that for a given metal ion the values for the ligands IDA⁻² and PG⁻² are very similar. This observation provides highly compelling evidence that the pyruvate and glycinate in the mixed complexes are condensed in a 1:1 ratio producing, effectively, a tridentate ligand having two oxygen and one nitrogen donor atoms.

Nitrogen donors usually show a considerable difference between the stabilities of the Ca(II) and Zn(II) complexes (*e.g.*, no phen complex of Ca(II) is known), while oxygen donors usually exhibit only a slight increase in the stability of the Zn(II) complex relative to the Ca(II) (*e.g.*, see the values for pyruvate, Table I). The intermediate behavior of the IDA⁻² and PG⁻² complexes indicates a change from predominant oxygen bonding with Ca(II) to predominant nitrogen bonding with Zn(II).

On forming higher species with a given metal ion, the stepwise constants for the complexes with saturated

ligands remain at about the same level, or show a progressive decrease after correcting for statistical effects. This trend can be noted in the figures in Table III for the glycinate and IDA⁻² complexes. On the other hand, after correction, the phen complexes actually show an increase in stability with increasing coordination. This latter effect is attributed to an increase in the metal-nitrogen bond strength when the region oc-

cupied by these atoms becomes progressively shielded from the high dielectric solvent as the degree of coordination increases. This effect tends to exist with saturated ligands but is more important with the more polarizable donor atoms.¹⁷ The PG⁻² complexes follow phen in this respect, giving further evidence for the presence of unsaturated nitrogen.

The positions of the spectral band maxima for the Ni(II) complexes in the visible and near-infrared regions are reported in Table IV. The spectrum of NiP⁺ is

TABLE IV

SPECTRAL BAND MAXIMA OF SOME Ni(II) COMPLEXES

	ν ₁	ν ₂	ν ₃	ν ₄
Ni(H ₂ O) ₆ ⁺²	8,470	13,900	15,240	25,320
NiP ⁺	8,550	13,800	15,090	25,380
NiPG	9,660	...	15,700	27,000 sb
NiPG ₂ ⁻	10,060	...	16,300	...
NiP ₂ G ₂ ⁻²	10,260	...	16,330	...
NiG ⁺	9,660	13,790 sh	15,530	26,180
NiG ₂ ^a	9,900	13,300	16,230	27,100
NiG ₃ ⁻	10,000	13,100	16,560	27,590
Ni(en) ^{+2b}	10,300	13,600	16,020	26,900
Ni(en) ₃ ⁺²	11,200	12,400	18,350	29,000
Ni(phen) ^{+2b}	10,050	13,700	16,250	27,000
Ni(phen) ₃ ^{+2c}	12,700	11,500	19,300	...

^a The solution from which these data were obtained also contained small amounts of NiG⁺ and NiG₃⁻ arising from the disproportionation of NiG₂. ^b Spectra obtained from solutions in which the metal-to-ligand ratio was at least 5:1. The spectrum of the excess Ni(II) was subtracted by placing in the reference beam a matched cell containing a solution having a concentration identical with the excess Ni(II). ^c Band assignments are those reported in ref. 18; for further verification, see also M. A. Robinson, J. D. Curry, and D. H. Busch, *Inorg. Chem.*, **2**, 1178 (1963).

very much like that of the aquo ion but with a slight intensification of the bands and a very slight shift to higher energies. The glycinate complexes show the well-known shifts to higher frequencies brought about by nitrogen coordination and also show further increases in intensity. The position of ν₁ for NiPG almost exactly coincides with the position of ν₁ in NiG⁺. Each of these species contains only one coordinated nitrogen. The relative positions of ν₂ and ν₃ in these two complexes

(17) D. L. Leussing, *Inorg. Chem.*, **2**, 77 (1963); R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

suggest a slightly lower degree of covalency in the mixed complexes.¹⁸

Interestingly, the higher mixed species show somewhat greater shifts than are observed for the simple glycinate complexes so that the position of ν_1 in $\text{NiP}_2\text{G}_2^{-2}$, with only two nitrogen atoms, is significantly higher than ν_1 in even NiG_3^- . Also, comparing these two ions, the lower ν_3/ν_1 ratio in $\text{NiP}_2\text{G}_2^{-2}$ shows that $\text{NiP}_2\text{G}_2^{-2}$ possesses a higher degree of covalency.¹⁸

Similar behavior is noted in the en and phen complexes of Ni(II). In the 1:1 complex, phen is seen to have an influence that is less than, or about equal to, that of en. In the tris complex, however, phen exerts by far the more powerful field. These trends parallel those noted above in the discussion of the stabilities and are further evidence that polarizable ligands have the greatest effect on metal ions when the degree of complexing is the highest.

The ultraviolet spectra of these complexes are also interesting. The Mn(II)-PG solutions exhibit an intense absorption band centered at about $31,000\text{ cm}^{-1}$ ($\epsilon \sim 10^4$). This band is unlike those of free pyruvate or of the Ni(III) complexes. A tentative explanation is that this Mn band represents charge transfer of electrons from metal to ligand π^* -orbitals with the resulting Mn(III) state being stabilized by the coordinated carboxylate oxygen atoms.

The heats and entropy contributions calculated from the data of Table I are presented in Table V. The heat

TABLE V
APPROXIMATE HEAT AND ENTROPY CONTRIBUTIONS TO
COMPLEX FORMATION^a

$$\text{M}^{+2} + p\text{P}^- + g\text{G}^- \xrightarrow{25^\circ} \text{MP}_p\text{G}_g$$

Complex	Mn		Ni		Zn	
	ΔH	$T\Delta S$	ΔH	$T\Delta S$	ΔH	$T\Delta S$
MG ⁺	-1.4	2.2	-1.9	5.9	-2.1	4.6
MG ₂ ⁰	-3.3	2.9	-7.5	6.8	-5.9	6.4
MPG ⁰	-4.0	3.3	-2.6	8.5	-1.9	8.4
MP ₂ G ₂ ⁻²	-11.8	1.6	-11.9	9.0	-7.5	12.0

^a Units in kcal./mole.

of K_{2a} for glycine is calculated to be 11.0 kcal./mole, which is in excellent agreement with the value 10.8 kcal./mole reported by King.¹⁹ However, the precision of the

results decreases rapidly as the complexity of the system increases. The heats given in Table V for the formation of the glycinate complexes are only in fair agreement with those recently reported,²⁰ although it should be noted that the extrapolation of our results to the zero ionic strength values reported in ref. 20 has a far greater effect on the values than the 15° temperature change examined here.

Within the uncertainty of perhaps 1 or 2 kcal./mole, it is apparent that the entropy contributions are an important factor in stabilizing the Schiff base complexes of Ni(II) and Zn(II). At least with the former ion this is also implied in the observations that the ligand field strengths in NiG⁺ and NiPG are comparable, but the constant for the binding of G⁻ to NiP⁺ is 20 times greater than the constant for the binding of G⁻ to Ni(H₂O)₆⁺². The entropy contributions do not seem to be as important with Mn(II). Qualitatively this is in agreement with the other evidence which shows that essential differences exist between the Ni(II) and Zn(II) complexes, on the one hand, and those of Mn(II), on the other. This difference appears to have its origins in the relative proclivities of these ions for oxygen and nitrogen.

It is seen from this and earlier work^{1,4,5,7} that complexes having high stabilities are formed by metal ions in the presence of oxo and amino acids. These complexes mediate the transamination process in simple model systems and may also do so under biological conditions. Another intriguing consideration is the role that species such as these might play in metal ion transport systems. Since amino acids and oxo acids are intimately involved in the metabolic pathways, it should be possible to bring these components together in situations which require a ligand having the complexing ability of a tridentate ligand, or greater. When this strong complexor is no longer required, it can be easily destroyed through well-known pathways. Evidence involving such a mechanism already exists for amino acid transport into cells.²¹

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