must exist. Also, on deprotonation to give Ni(H_2O)-(EDTA)$^{2-}$, the $k_1(25°)$ goes up to 7×10^5 and $\Delta H^{\ddagger}$ goes down to 8.0, which facts suggest that the acetate arms do interact significantly with nickel and/or that solvation and entropy effects are also important. At 25° the labilizing effects of ligands correlate roughly with their electron-donating or -accepting properties but, as discussed in ref 19, the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are difficult to rationalize on this basis alone.

Acknowledgment. This work was supported in part by Contract No. AT(45-1)-2221 with the U. S. Atomic Energy Commission and by funds provided by the Washington State University Graduate School from a National Science Foundation Institutional Grant.

Reaction of Ethylenediamine and *C,C,C′,C′*-Tetramethylethylenediamine with Glyoxylate in the Presence and Absence of Zinc(II) or Nickel(II)[1]

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Abstract: Glyoxylate reacts with ethylenediamine dihydrochloride (en·2HCl) and *C,C,C′,C′*-tetramethylethylenediamine dihydrochloride (temeen·2HCl) to form 1:1 adducts which are considerably more stable and acidic than Schiff bases. These adducts also form complexes with Ni(II) and Zn(II) which are less stable than Schiff base complexes. These results suggest that cyclic imidazolidine structures are formed. Proton magnetic resonance spectra confirm this conclusion. In the presence of a complexing metal ion and excess glyoxylate, the ring of 2-carboxylate imidazolidine opens up to form a quadridentate ligand. Formation constants for these species are reported.

Investigations underway in this laboratory regarding the kinetic and equilibrium properties of aqueous solutions of Schiff base complexes are extended in this work to diamine systems. The reactions of ethylenediamine (en) and *C,C,C′,C′*-tetramethylethylenediamine (temeen) with glyoxylate (glyox$^-$) are reported here.

Glyoxylate was chosen for this initial study of diamine behavior because it reacts rapidly and cleanly with amines in aqueous solution,[2] does not dimerize as does pyruvate,[3] and is less likely to give the problems with insolubility which arise with the aromatic aldehydes.

It had been found earlier[2] that glyoxylate reacts with α-alaninate to form a Schiff base.

$$CH_3CH(NH_2)CO_2^- + HCOCO_2^- \longrightarrow CH_3CH(N{=}CHCO_2^-)CO_2^- + H_2O \quad (1)$$

With glycinate, however, the glyoxylate adduct appears to be extensively hydrated as the carbinolamine.[2]

$$NH_2CH_2CO_2^- + HCOCO_2^- \longrightarrow CH_2(NHCHOHCO_2^-)CO_2^- \quad (2)$$

The diamines can react in similar ways and, because a second primary amine group is available, can also add a second glyoxylate to give a bis Schiff base

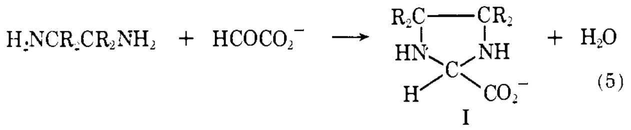
$$NH_2CR_2CR_2N{=}CHCO_2^- + HCOC_2^- \longrightarrow {}^-O_2CCH{=}NCR_2CR_2N{=}CHCO_2^- + H_2O \quad (3)$$

or a bis carbinolamine

$$NH_2CR_2CR_2NHCH(OH)CO_2^- + HCOCO_2^- \longrightarrow {}^-O_2CH(OH)NHCR_2CR_2NHCH(OH)CO_2^- \quad (4)$$

Reactions 3 and 4 yield quadridentate ligands as products, and it was anticipated that the presence of complexing metal ions would promote reactions along these paths.

In addition to the above reactions, cyclic structures may also be formed between polyfunctional amines and carbonyl compounds.[4–8] Pertinent to the present work, cyclization between en or temeen and glyoxylate would lead to an imidazolidine-2-carboxylate.[4]



(5)

The present study was undertaken to determine which of the above diamine–glyoxylate addition reactions are

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(1) The authors wish to express their appreciation to the National Science Foundation for their support of this research.

(2) D. L. Leussing and E. M. Hanna, *J. Amer. Chem. Soc.*, **88**, 696 (1966).

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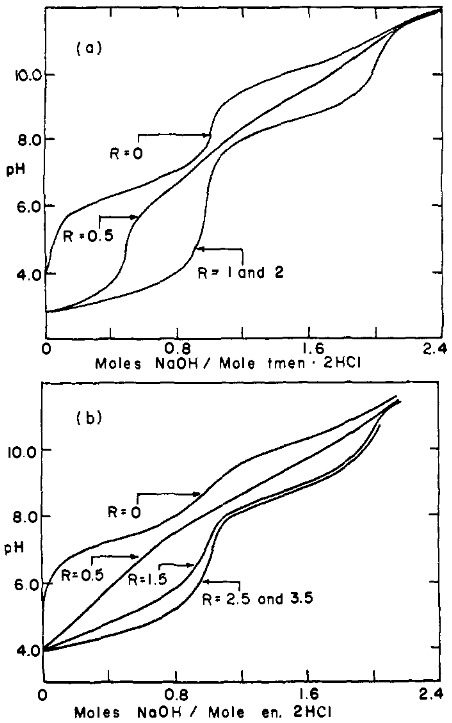

Figure 1. Titration of 0.050 *M* diamine·2HCl in the presence of glyoxylate; *R* = moles of Na glyox per mole of diamine: (a) *C,C,C',C'*-tetramethylethylenediamine·2HCl, (b) ethylenediamine·2HCl; ionic strength = 1.0, 25°.

Table I. Ligand Protonation and Binary Complex Formation Constants[a]

Glyoxylate	
$H^+ + glyox^- \rightleftarrows Hglyox$	Log K_1 = 2.91
$Ni^{2+} + glyox^- \rightleftarrows Ni(glyox)^+$	Log β_1 = 1.06
$Ni^{2+} + 2glyox^- \rightleftarrows Ni(glyox)_2$	Log β_2 = 1.32
$Zn^{2+} + glyox^- \rightleftarrows Zn(glyox)^+$	Log β_1 = 1.06
$Zn^{2+} + 2glyox^- \rightleftarrows Zn(glyox)_2$	Log β_2 = 1.68
Ethylenediamine	
$H^+ + en \rightleftarrows Hen^+$	Log K_1 = 10.16
$H^+ + Hen \rightleftarrows H_2en^{2+}$	Log K_{12} = 7.41
$Ni^{2+} + en \rightleftarrows Ni(en)^{2+}$	Log β_1 = 7.60[b]
$Ni^{2+} + 2en \rightleftarrows Ni(en)_2{}^{2+}$	Log β_2 = 14.80[b]
$Ni^{2+} + 3en \rightleftarrows Ni(en)_3{}^{2+}$	Log β_3 = 19.11[b]
$Zn^{2+} + en \rightleftarrows Zn(en)^{2+}$	Log β_1 = 5.92[b]
$Zn^{2+} + 2en \rightleftarrows Zn(en)_2{}^{2+}$	Log β_2 = 11.07[b]
$Zn^{2+} + 3en \rightleftarrows Zn(en)_3{}^{2+}$	Log β_3 = 12.93[b]
C,C,C',C'-Tetramethylethylenediamine	
$H^+ + temeen \rightleftarrows Htemeen^+$	Log K_1 = 10.10
$H^+ + Htemeen^+ \rightleftarrows H_2temeen^{2+}$	Log K_{12} = 6.46
$Ni^{2+} + temeen \rightleftarrows Ni(temeen)^{2+}$	Log $\beta_1 < 6$[b]
$Ni^{2+} + 2temeen \rightleftarrows Ni(temeen)_2{}^{2+}$	Log β_2 = 14.56[b]
$Zn^{2+} + temeen \rightleftarrows Zn(temeen)^{2+}$	Log β_1 = 6.32[b]
$Zn^{2+} + 2temeen \rightleftarrows Zn(temeen)_2{}^{2+}$	Log β_2 = 14.56[b]

[a] Ionic strength 1.0, 25°. [b] D. L. Leussing, *Inorg. Chem.*, **2**, 77 (1963).

important in aqueous solutions and the effect of metal ions upon them. To follow the reactions, the pH titration technique[2] was employed in conjunction with proton magnetic resonance measurements.

Results

In order to analyze the data obtained in this study it is necessary to have the formation constants for various binary species which may be present. These required protonation and complexation constants are given in Table I.

Curves of pH *vs.* mole ratio for the titration of 0.050 *M* temeen·2HCl with standard NaOH in the presence of 0, 0.025, 0.050, and 0.10 *M* Na glyox at an ionic strength of 1.0 at 25° are shown in Figure 1a. Here it can be observed that the presence of glyox⁻ markedly depresses (by about 2.5–3 pH units) the region for the neutralization of the first proton

$$^{2+}H_2temeen + OH^- \longrightarrow {}^{+}Htemeen + H_2O$$

The pH region for the neutralization of the second proton

$$^{+}Htemeen + OH^- \longrightarrow temeen + H_2O$$

is also seen to be depressed (by about 1.5 pH units).

When the molar ratio of glyox:temeen is less than 1:1, a sharp break is observed in the titration curve at a point which corresponds to an amount of NaOH equimolar to the Na glyox present. When the glyox:temeen ratio is 1:1 or greater, this break corresponds to the neutralization of the first temeem·2HCl proton. Equilibrium times before this first end point were found to be of the order of 10 min. Past this end point equilibration times are a few seconds and are determined by the response time of the pH meter and electrode system to changes in pH.

These results show that in the region before and up to the first end point at pH ~5 a strong temeen–glyox adduct is formed according to the reaction[9]

$$OH^- + H_2temeen^{2+} + glyox^- \xrightarrow{slow} H(temeen\cdot glyox) + H_2O \quad (6)$$

After the first end point in the pH range 8–10, the remaining bound proton undergoes neutralization

$$H(temeen\cdot glyox) + OH^- \xrightarrow{fast} (temeen\cdot glyox)^- + H_2O \quad (7)$$

Reaction 6 tends to lie too far to the right under the conditions described in the legend of Figure 1 to give accurate equilibrium constants, so in order to obtain better data it was necessary to shift reaction 6 to the left by increasing the acidity of the solutions. This was done by having glyoxylic acid present initially rather than glyoxylate ions. Details of the titrations are provided in the Experimental Section. With this modification, satisfactory equilibrium data were obtained. Numerical analyses of these data indicated not only the formation of H(temeen·glyox) and (temeen·glyox)⁻, which were deduced above, but also the formation of a third species, $H_2(temeen\cdot glyox)^+$ according to the reaction

$$H_2temeen^{2+} + Hglyox + {}^-OH \xrightarrow{slow} H_2(temeen\cdot glyox)^+ + H_2O \quad (8)$$

The formation constants for these adducts are given in Table II.

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(9) The number of water molecules involved in the reaction is not provided by the equilibrium data so has been omitted from the equation.

Table II. Mixed Ligand and Ternary Complex Formation Constants[a]

Reaction	Constant
C,C,C′,C′-Tetramethylethylenediamine–Glyoxylate	
$\mathrm{temeen} + \mathrm{glyox}^- \rightleftarrows (\mathrm{temeen}\cdot\mathrm{glyox})^{-\,b}$	$\mathrm{Log}\ \beta_{\mathrm{tg}} = 6.70$
$\mathrm{H}^+ + (\mathrm{temeen}\cdot\mathrm{glyox})^- \rightleftarrows \mathrm{H}(\mathrm{temen}\cdot\mathrm{glyox})$	$\mathrm{Log}\ K_1 = 8.66$
$\mathrm{H}^+ + \mathrm{H}(\mathrm{temeen}\cdot\mathrm{glyox}) \rightleftarrows \mathrm{H}_2(\mathrm{temeen}\cdot\mathrm{glyox})^+$	$\mathrm{Log}\ K_{12} = 2.69$
$\mathrm{Ni}^{2+} + (\mathrm{temeen}\cdot\mathrm{glyox})^- \rightleftarrows \mathrm{Ni}(\mathrm{temeen}\cdot\mathrm{glyox})^+$	$\mathrm{Log}\ \beta_1 = 2.94$
$\mathrm{Ni}^{2+} + 2(\mathrm{temeen}\cdot\mathrm{glyox})^- \rightleftarrows \mathrm{Ni}(\mathrm{temeen}\cdot\mathrm{glyox})_2$	$\mathrm{Log}\ \beta_2 = 6.74$
$\mathrm{H}^+ + \mathrm{Ni}(\mathrm{temeen}\cdot\mathrm{glyox})^+ \rightleftarrows \mathrm{HNi}(\mathrm{temeen}\cdot\mathrm{glyox})^{2+}$	$\mathrm{Log}\ K_1 = 6.86$
$\mathrm{Zn}^{2+} + (\mathrm{temeen}\cdot\mathrm{glyox})^- \rightleftarrows \mathrm{Zn}(\mathrm{temeen}\cdot\mathrm{glyox})^+$	$\mathrm{Log}\ \beta_1 = 3.24$
$\mathrm{Zn}^{2+} + 2(\mathrm{temeen}\cdot\mathrm{glyox})^- \rightleftarrows \mathrm{Zn}(\mathrm{temeen}\cdot\mathrm{glyox})_2$	$\mathrm{Log}\ \beta_2 = 6.38$
$\mathrm{H}^+ + \mathrm{Zn}(\mathrm{temeen}\cdot\mathrm{glyox})^+ \rightleftarrows \mathrm{HZn}(\mathrm{temeen}\cdot\mathrm{glyox})^{2+}$	$\mathrm{Log}\ K_1 = 6.34$
Ethylenediamine–Glyoxylate	
$\mathrm{en} + \mathrm{glyox}^- \rightleftarrows (\mathrm{en}\cdot\mathrm{glyox})^{-\,b}$	$\mathrm{Log}\ \beta_{\mathrm{eg}} = 5.01$
$\mathrm{H}^+ + (\mathrm{en}\cdot\mathrm{glyox})^- \rightleftarrows \mathrm{H}(\mathrm{en}\cdot\mathrm{glyox})$	$\mathrm{Log}\ K_1 = 8.85$
$\mathrm{H}^+ + \mathrm{H}(\mathrm{en}\cdot\mathrm{glyox}) \rightleftarrows \mathrm{H}_2(\mathrm{en}\cdot\mathrm{glyox})^+$	$\mathrm{Log}\ K_{12} = 1.95$
$\mathrm{Ni}^{2+} + (\mathrm{en}\cdot\mathrm{glyox})^- \rightleftarrows \mathrm{Ni}(\mathrm{en}\cdot\mathrm{glyox})^+$	$\mathrm{Log}\ \beta_1 = 7.10$
$\mathrm{Ni}^{2+} + 2(\mathrm{en}\cdot\mathrm{glyox})^- \rightleftarrows \mathrm{Ni}(\mathrm{en}\cdot\mathrm{glyox})_2$	$\mathrm{Log}\ \beta_2 = 12.2$
$\mathrm{H}^+ + \mathrm{Ni}(\mathrm{en}\cdot\mathrm{glyox})^+ \rightleftarrows \mathrm{HNi}(\mathrm{en}\cdot\mathrm{glyox})^{2+}$	$\mathrm{Log}\ K_1 = 5.05$
$\mathrm{Ni}(\mathrm{en}\cdot\mathrm{glyox})^+ + \mathrm{glyox}^- \rightleftarrows \mathrm{Ni}(\mathrm{en}\cdot\mathrm{glyox}_2)^b$	$\mathrm{Log}\ K_1 = 2.45$
$\mathrm{Zn}^{2+} + (\mathrm{en}\cdot\mathrm{glyox})^- \rightleftarrows \mathrm{Zn}(\mathrm{en}\cdot\mathrm{glyox})^+$	$\mathrm{Log}\ \beta_1 = 5.28$
$\mathrm{Zn}^{2+} + 2(\mathrm{en}\cdot\mathrm{glyox})^- \rightleftarrows \mathrm{Zn}(\mathrm{en}\cdot\mathrm{glyox})_2$	$\mathrm{Log}\ \beta_2 = 9.05$
$\mathrm{H}^+ + \mathrm{Zn}(\mathrm{en}\cdot\mathrm{glyox})^+ \rightleftarrows \mathrm{HZn}(\mathrm{en}\cdot\mathrm{glyox})^{2+}$	$\mathrm{Log}\ K_1 = 5.86$
$\mathrm{Zn}(\mathrm{en}\cdot\mathrm{glyox})^+ + \mathrm{glyox}^- \rightleftarrows \mathrm{Zn}(\mathrm{en}\cdot\mathrm{glyox}_2)^b$	$\mathrm{Log}\ K_1 = 1.92$

[a] Ionic strength 1.0 (NaCl), 25°. [b] The number of water molecules released in the reaction is not given by the data, so has been omitted from the equations.

Proton magnetic resonance spectra of a 1:1 temeen·2HCl–glyox$^-$ mixture as a function of degree of neutralization are shown in Figure 2. The band at 100.1 cps (*vs.* internal $\mathrm{Me_4N^+Cl^-}$) corresponds to the resonance of the magnetically equivalent methyl protons of free $\mathrm{H_2temeen^{2+}}$[10] as determined from experiments in the absence of glyox$^-$. The additional band which appears at 109.6 Hz in the initial solution before NaOH is added ($N = 0$) corresponds to the average of the resonances of the methyl protons of the adducts $\mathrm{H_2}$(temeen·glyox) and H(temeen·glyox)$^-$ which are formed to an appreciable extent under these conditions. As NaOH is added and reactions 6 and 8 are shifted to the right, the band arising from free $\mathrm{H_2temeen^{2+}}$ is seen in Figure 2 to diminish in intensity while the intensity of the adduct band increases. Simultaneously, the position of the adduct band undergoes a slight upfield shift owing to the formation of a higher proportion of H(temeen·glyox)$^-$. By the time the first end point is reached, the free $\mathrm{H_2temeen^{2+}}$ has quantitatively reacted with glyox$^-$ and only the methyl resonance of H(temeen·glyox) is observed. This band undergoes a further upfield shift with increasing pH as H(temeen·glyox) is converted to (temeen·glyox)$^-$. If instead of NaOH, HCl is added to the initial solution, the adduct band undergoes a slight downfield shift and decreases in intensity with decreasing pH. This behavior arises both from an increase in the percentage of adduct which is present as $\mathrm{H_2}$(temeen·glyox)$^+$ as the pH decreases and dissociation

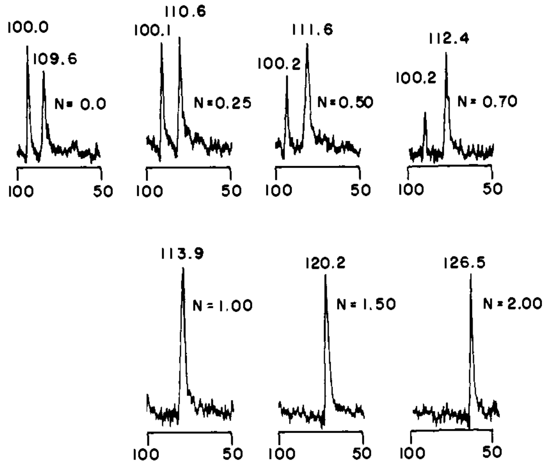

Figure 2. Methyl proton magnetic resonance spectra (60 MHz) for the neutralization of *C,C,C′,C′*-tetramethylethylenediamine dihydrochloride (0.10 *M*) in the presence of sodium glyoxylate (0.10 *M*); N = moles of NaOH per mole of diamine. The numbers above each peak give the chemical shift upfield with respect to internal $\mathrm{(CH_3)_4N^+Cl^-}$. The numbers below the abscissa are the shifts downfield from external TMS.

$$\mathrm{H_2(temeen\cdot glyox)^+ + H^+ \longrightarrow Hglyox + H_2temeen^{2+}}$$

By pH 1.9, the adduct band has completely disappeared and only the resonance of free $\mathrm{H_2temeen^{2+}}$ is observed.

These pmr results verify the conclusions obtained from the pH data that $\mathrm{H_2temeen^{2+}}$ and glyox$^-$ react to form a stable addition product which can lose two protons in discrete steps, but no species such as $\mathrm{H_3}$(temeen·glyox)$^{2+}$ is formed. The dependence on pH of the position of the adduct methyl resonance both before and after the first end point is evidence that it is both of the nitrogen atoms of the adduct which are protonated. In each of the possible structures presented above, the carboxylate group is sufficiently far removed from the methyl groups that its protonation would have a much smaller effect on the methyl resonances than is observed.

The pH titration curves for the en·2HCl–glyox system are shown in Figure 1b. The curves show similar behavior to that obtained for the temeen–glyox system, but the distortion and the poorly resolved first end point (until excess Na glyox is present) show that the affinity of glyox$^-$ for en is substantially lower than for temeen. The analysis of the Hglyox–en·2HCl titration data indicated the formation of adducts analogous to those above: $\mathrm{H_2}$(en·glyox)$^+$, H(en·glyox), and (en·glyox)$^-$. The formation constants of these species are also given in Table II.

The methylene proton magnetic resonance spectra for en–glyox mixtures (Figure 3) are qualitatively similar to those shown in Figure 2 for temeen–glyox. Weaker interactions and exchange broadening affect the curve shapes at values of pH below those of the first end point, however.

The effect of added Ni(II) or Zn(II) on the temeen–glyox titration curves is to slightly depress the pH region for the neutralization of the first proton of $\mathrm{H_2}$(temeen·glyox)$^+$ (by less than 0.1 pH unit), whereas in the second plateau region, which corresponds to the formation of

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[10] The positions of the methyl proton resonances of free temeen are $\mathrm{H_2temeen^{2+}}$, 100.4 ± 0.2; $\mathrm{Htemeen^+}$, 107.1 ± 0.2; temeen, 124.9 ± 0.2 Hz upfield from $\mathrm{Me_4N^+Cl^-}$.

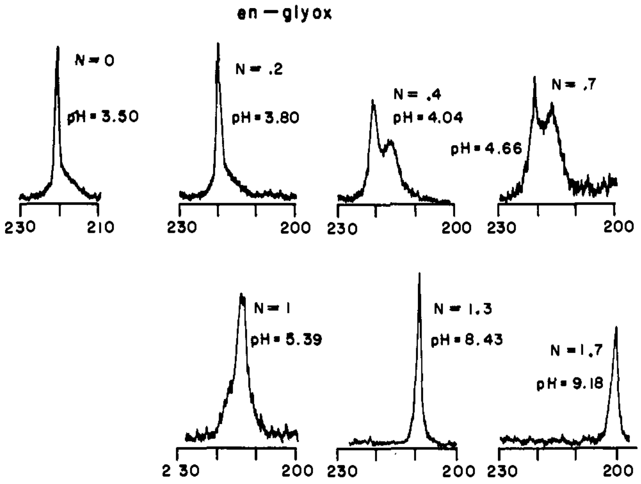


Figure 3. Methylene proton magnetic resonance spectra (60 MHz) for the neutralization of ethylenediamine dihydrochloride (0.10 *M*) in the presence of sodium glyoxylate (0.10 *M*); *N* = moles of NaOH per mole of diamine. The numbers below the abscissa are the shifts downfield from external TMS.

(temeen · glyox)⁻, the pH is lowered by 1–2 units. Thus, the divalent metal ions interact weakly with H(temeen · gly) and more strongly with (temeen · glyox)⁻. Precipitation occurred in the region 6.5–7 with Zn(II) and around pH 8 with Ni(II). In spite of these solubility difficulties, sufficient data were obtained to demonstrate the formation of the species M(temeen · glyox)⁺, M(temeen · glyox)$_2$, and MH(temeen · glyox)$^{2+}$ and to yield satisfactory formation constants for them (Table II).

In the en–glyox system the presence of Ni(II) or Zn(II) caused the first neutralization region to be lowered by about 1 pH unit. Furthermore, the acidity of the second plateau region was enhanced so that the break at the first end point was obliterated. Quite obviously, stronger M(II)–adduct interactions exist than in the temeen–glyox system. Precipitation with both metal ions around pH 6 did not preclude the acquisition of pertinent equilibrium data, however. Analysis indicated the formation of the same types of species found above, M(en · glyox)⁺, M(en · glyox)$_2$, and M(en · glyox)H⁺; however, these species alone could not account for a distortion to lower pH which was observed for the curves obtained from the solutions containing higher concentrations of glyoxylate. This distortion was well outside the experimental uncertainties and amounted to several tenths of a pH unit. The nature of the effect suggests the formation of M(en · glyox$_2$) and with the inclusion of this species it was possible to fit theoretical curves to those observed. The formation constants which were obtained are given in Table II.

Discussion

The logarithms of the equilibrium constants for reactions 1 and 2 are 1.27 and 1.75.[2] In contrast to these are the relatively high values found here for the diamine–glyox interactions

$$\text{temeen} + \text{glyox}^- \rightleftharpoons (\text{temeen}\cdot\text{glyox})^- \qquad \log \beta_{\text{tg}} = 6.70$$

and

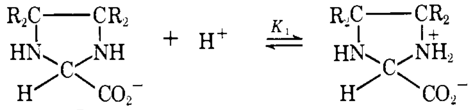
$$\text{en} + \text{glyox}^- \rightleftharpoons (\text{en}\cdot\text{glyox})^- \qquad \log \beta_{\text{eg}} = 5.01$$

The formation constants given for reactions 1 and 2 are typical of those for Schiff base formation; similar values have been reported for the interaction of various primary monoamines with pyruvate,[11] salicylaldehyde,[12] and pyridoxal.[13] Thus, the diamine–glyoxylate interactions encountered here appear to be fundamentally different from those characteristic of Schiff base formation.

Other evidence that Schiff bases are not formed is obtained from the pmr spectra. The pmr spectra of solutions which contain both glyoxylate and α-alaninate show clearly resolved methyl resonances (Δ 13 cps) of the $CH_3CN=$ group of glyoxylidenealaninate and the CH_3CNH_2 group of unreacted α-alaninate.[14] Therefore, if the 1:1 temeen–glyox⁻ adduct had a Schiff base structure, $NH_2C(Me)_2C(Me)_2N{=}CHCO_2^-$, two sets of magnetically nonequivalent methyl protons should be clearly discernible in the pmr spectrum. A hydrated carbinolamine structure should also be recognizable through the appearance of nonequivalent protons. To the contrary, both the temeen and en adducts of glyoxylate show essentially magnetically equivalent carbon protons.

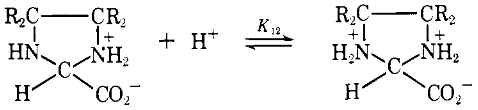
More consistent with the experimental results is the formation of cyclic imidazolidines (reaction 5) rather than Schiff bases or carbinolamines. The high stability of the temeen derivative further supports the assignment of a cyclic structure, since the influence of the methyl substituents is to enhance the stability of the ring.[15]

Further evidence for imidazolidine ring formation is contained in the observed protonation constants of the adducts. Using the rules set forth by Clark and Perrin,[16] it can be estimated that successive protonation of the imine groups of I should take place with log K_1 equal to about 8

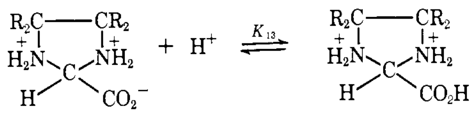


I

with log K_{12} lying in the range 1–3



Protonation of the 2-carboxylate group should correspond to log K_{13} of about zero



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[11] D. L. Leussing and D. C. Schultz, *J. Amer. Chem. Soc.*, **86**, 4846 (1964).

[12] D. L. Leussing and K. S. Bai, *Anal. Chem.*, **40**, 575 (1968).

[13] D. L. Leussing and N. Huq, *ibid.*, **38**, 1388 (1966).

[14] D. L. Leussing and C. S. Stanfield, *J. Amer. Chem. Soc.*, **86**, 2805 (1964).

[15] E. L. Eliel, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956.

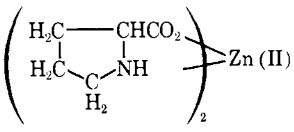
[16] J. Clark and D. D. Perrin, *Quart. Rev., Chem. Soc.*, **18**, 295 (1964).

These estimates are in reasonable agreement with the observations. On the other hand, protonation of a Schiff base

$$H^+ + H_2NCH_2CH_2N{=}CHCO_2^- \rightleftarrows H_3^+NCH_2CH_2N{=}CHCO_2^-$$

should give rise to a log K_1 close to that of the parent amine, *i.e.*, around 10. Log K_{12} should lie in the range 3–6 and log K_{13} should be of the order 0–1. The first two of these latter estimates are clearly not in agreement with the observations.

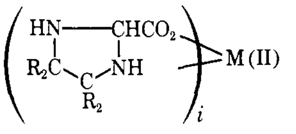
The affinities of the adducts for metal ions are also not typical of those expected for Schiff bases. The amino acid Schiff bases involving polyfunctional carbonyl compounds characteristically form more stable complexes than do the parent amino acids owing to a higher number of chelate rings provided by the Schiff bases. For example, log β_1 is 3.8 for the reaction $Zn^{2+} + L \rightleftarrows ZnL^{2+}$, when L is glycinate ($gly^-$),[17] but when L is the adduct $(gly \cdot glyox)^{2-}$, log β_1 is 4.9.[2] The relative stabilities are reversed for the present systems: log β_1 is 5.9 for Zn^{2+}–en, but only 4.9 for Zn^{2+}–$(en \cdot glyox)^-$ and is 6.3 for Zn^{2+}–temeen, but only 3.2 for Zn^{2+}–$(temeen \cdot glyox)^-$. Furthermore, the stabilities of the Zn^{2+}–$(en \cdot glyox)^-$ species fall into line with those for Zn(II)–proline[17] after taking into account the effect of the greater proline basicity.



log $\beta_2 = 10.2$
log $K_{1H} = 10.7$

Thus, several lines of evidence, the stabilities of the diamine–glyoxylate adducts and the influence of carbon methyl substituents upon them, the reaction rates, proton magnetic spectra, and the stabilities and reactivities of the metal complexes, are consistent with the formation of cyclic imidazolidine structures in aqueous solutions.

The 1:1:1 and 1:2:2 metal ion–diamine–glyoxylate complexes are assigned the structures

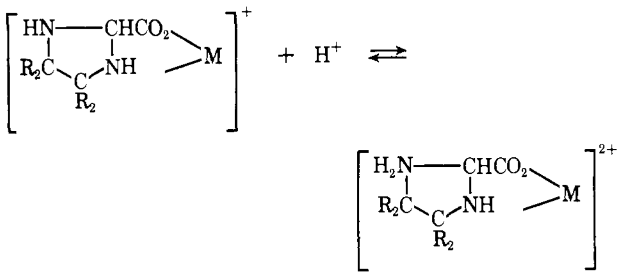


$i = 1, 2$

Pmr spectra of solutions of the Zn(II) complexes verify these structures, since the carbon protons of the complexed adducts are all found to be magnetically equivalent just as in the absence of metal ions.

The stabilities of the $(temeen \cdot glyox)^-$–Ni(II) and Zn(II) complexes are somewhat low, likely from metal–ligand steric repulsions which arise from the presence of the methyl groups. The inverted order of stabilities with this ligand, Ni(II) < Zn(II), are a further indication of steric hindrance of this type.[18,19]

The complexed imidazolidine has a free imine group which is able to accept a proton



The log K values for this protonation (Table II) lie in the inverse order of the stabilities of the *unprotonated* complexes.

$$\xrightarrow{\text{increasing stability of complex}}$$
$$\xleftarrow[\text{increasing basicity of imine group}]{}$$

$Ni(temeen \cdot glyox)^+$, $Zn(temeen \cdot glyox)^+$,
$Zn(en \cdot glyox)^+$, $Ni(en \cdot glyox)^+$

Since the electrostatic effect of the divalent metal ion remains essentially constant throughout this series, this inverse dependence must necessarily reflect differences in the inductive effects which are exerted by the coordinated metal ions on the far imine nitrogen: the greater the interaction between the carboxylate group and an imine nitrogen, the lower is the electron density on the far nitrogen. On the other hand, while these inductive effects are appreciable, they appear to be considerably smaller in these ring systems than are the inductive effects exerted by the proton. The logarithms of the protonation constants for the free imine nitrogen are 6.34–6.86 for $M^{II}(temeen \cdot glyox)^+$. However, the analogous protonation constants for $H(temeen \cdot glyox)$ and $H(en \cdot glyox)$ are log 2.69 and 1.95. Thus, in spite of an additional electrostatic contribution in the case of the metal ions, the availability of electrons on the free imine group is seen to be considerably lower with the monoprotonated uncomplexed ligands.

The M(II)–en–glyox system forms species in which the M(II):en:glyox⁻ ratio is 1:1:2. The stepwise constants in Table II for the acquisition of the second glyoxylate by the metal ion complexes

$$M(en \cdot glyox)^+ + glyox^- \rightleftarrows M(en \cdot glyox_2)$$
$$\log K = 2.45\ (Ni)$$
$$= 1.92\ (Zn)$$

are one to two orders of magnitude greater than are the analogous constants in Table I for the binding of the glyoxylate to the simple metal ions

$$M^{2+} + glyox^- \rightleftarrows M(glyox)^+$$
$$\log K_1 = 1.06\ (Ni),\ 1.06\ (Zn)$$

$$M(glyox)^+ + glyox^- \rightleftarrows M(glyox)_2$$
$$\log K_2 = 0.26\ (Ni),\ 0.62\ (Zn)$$

This is strong evidence that the second glyoxylate reacts with the coordinated imidazolidine. The most

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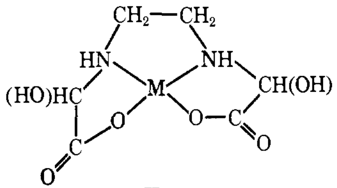
[17] L. G. Sillen and A. E. Martell, *Chem. Soc. Spec. Publ.*, **No. 17** (1964).

[18] D. L. Leussing, *Inorg. Chem.*, **2**, 77 (1963).

[19] F. Basolo, Y. T. Chen, and R. K. Murman, *J. Amer. Chem. Soc.*, **76**, 956 (1954).

plausible structure for the product is a quadridentate ligand, which, because of the absence of characteristic Schiff base absorbance at 230 nm, is likely the carbinolamine II.



II

This higher glyoxylate adduct is not observed with temeen. The high stability of the 4,4,5,5-tetramethylimidazoline-2-carboxylate ring plus steric interference in a higher glyox adduct likely inhibit the formation of a quadridentate ligand in the temeen–glyox system.

Experimental Section

Ethylenediamine, G. Frederick Smith Chemical Co., was fractionally distilled and converted to the dihydrochloride. *C,C,C′,C′*-Tetramethylethylenediamine was prepared by the Zn–HCl reduction of 2,3-dimethyl-2,3-dinitrobutane.[19,20] The redistilled amine was also converted to the dihydrochloride. The purities of these dihydrochlorides as determined by potentiometric titration with standard $AgNO_3$ were found to be better than 99.6%.

Crystalline Na(glyox)·H_2O was prepared from anhydrous sodium glyoxylate, Aldrich Chemical Co., by the method of Metzler, *et al.*[21] Analysis was performed by dissolving an accurately weighed quantity of the monohydrate in water, passing the solution through a cation-exchange column in the acid form (IR-120), and titrating the eluent with standardized NaOH solution. Purities of the order of 99.7–100.0% were indicated.

Equilibrium data were acquired from pH titration experiments performed on solutions at an ionic strength of 1.0 (NaCl) and at 25°. Test solutions under a blanket of nitrogen were titrated with either standard HCl or standard NaOH, depending on the experiment. Proton–glyoxylate and proton–diamine equilibrium constants as well as those for metal–glyoxylate interactions were determined under the conditions employed in this work. Metal ion–diamine complexity constants have been reported earlier.[18] Although the ionic strength in the earlier work[18] differs from that used here, the effect on the ternary constants reported above is negligible owing to the relatively low concentrations of the metal ion–diamine complexes in the glyoxylate–diamine–metal ion mixtures.

In the mixed glyoxylate–diamine or glyoxylate–diamine–metal ion solutions, the sodium glyoxylate was not added until just before the titration was performed so as to minimize the effects of any long-range side reactions. Where glyoxylic acid is reported to have been used, this was formed *in situ* by adding an accurately measured volume of standard HCl to the probe solution in an amount equivalent to and prior to the addition of the Na glyox.

Data for the mixed ligand systems in the absence of Ni(II) or Zn(II) were obtained by titrating the following solutions with standard 1.00 *M* NaOH (glyoxylic acid, *M*, diamine·2HCl, *M*): 0.100, 0.100; 0.200, 0.100; 0.150, 0.100; 0.100, 0.050; and 0.150, 0.050. Titrations in the presence of 0.025 *M* MCl_2 were performed at the following ligand levels (glyoxylic acid, *M*, diamine·2HCl, *M*): 0.050, 0.050; 0.025, 0.025; 0.050, 0.025; 0.100, 0.050 for Ni(II)–temeen and the Zn(II)- and Ni(II)–temeen and -en systems. Precipitation difficulties limited the range over which Zn(II)–temeen studies could be made. Titrations were performed on solutions 0.025 *M* in $ZnCl_2$ and 0.025, 0.035, 0.050, and 0.060 *M* in both glyoxylic acid and temen·2HCl. Precipitation occurred in the range pH 6.5–7. Ni(II) precipitation in the above solutions did not occur until pH ~8. Full details of the titrations are available elsewhere.[22]

The equilibrium constants were obtained using curve-fitting procedures similar to those which have been previously described.[11] With the constants reported below, it was possible to fit all curves with excellent agreement, the standard deviations being of the order of 0.02–0.03 pH unit over all titration curves.

A Radiometer PHM25a pH meter with a scale expander was employed for the hydrogen ion activity determinations. NBS buffers were used for standardization. In many of the experiments, the hydrogen ion concentration which appears in the mass balance expression was appreciable. Converson from the pH activity scale to concentration was done by determining the relationship between the pH meter reading and known H^+ concentration using standard HCl solutions at the same temperature and ionic strength.

Nmr spectra were obtained using a Varian A60 spectrometer.

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(20) L. W. Siegle and H. B. Hass, *J. Org. Chem.*, **5**, 100 (1940).

(21) D. E. Metzler, J. Olivard, and E. E. Snell, *J. Amer. Chem. Soc.*, **76**, 644 (1954).

(22) A. Hilton, Ph.D. Thesis, The Ohio State University, 1968.