NOTE ADDED IN PROOF.—L. H. Jones (*J. Chem. Phys.*, **23**, 2448 (1955)), has given the correct assignment for the $C^{13}{\equiv}O$ isotope band in the spectrum of $Ni(CO)_4$. But he erroneously implies that the intensity of the C^{13} band, (2022 cm.$^{-1}$), should be 4% of the intensity of the $Ni(C^{12}O)_4$ fundamental (2060 cm.$^{-1}$). The intensity of the fundamental is lessened by about 4.4% because of the natural abundance of $Ni(C^{13}O)(C^{12}O)_3$. But this C_{3v} molecule has three infrared-active CO stretching vibrations among which the intensity is distributed. Only 1 or 2% of the absorption intensity is expected to appear at the C^{13} band position, (2022 cm.$^{-1}$).

N. J. Hawkins, *et al.* (*J. Chem. Phys.*, **23**, 2422 (1955)), recently reported a detailed infrared and Raman spectral study of $Cr(CO)_6$. They incorrectly assigned the $C^{13}{\equiv}O$ isotope frequency at 1965 cm.$^{-1}$ as the second overtone of the 668 cm.$^{-1}$ vibration.

BRUCETON, PENNA.

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY OF LOUISIANA STATE UNIVERSITY]

The Stabilization of the Salicylaldehyde–Glycine Schiff Base through Metal Complex Formation[1,2]

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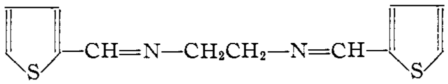
The coördination of copper(II) ion with the Schiff base produced from salicylaldehyde and glycine results in a stabilization of the double bond under conditions that would promote its rupture in the absence of the metal. The structural factors that determine whether metal coördination will stabilize or labilize Schiff bases are discussed. The composition of the complexes may be deduced from an extension of the method of continuous variation to a three-component complex system.

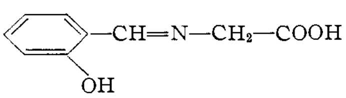
The participation of metal ions in many of the bond-forming and bond-breaking enzymatic processes of biochemistry makes it clear that individual chemical bonds in organic molecules are sometimes strengthened, and at other times weakened, through coördination of the molecules with metal ions. It is therefore of some interest to examine simple model systems to determine under what conditions metal complex formation affects molecules in these antithetical ways.

The Schiff bases constitute a series of molecules that appear well suited to serve in such model systems, since their carbon–nitrogen double bonds are susceptible both to hydrolytic cleavage and to coördination with metal ions. It has been demonstrated[3] that the double bond in 2-thiophenal-ethylenediamine is weakened by metal coördination;



A

the present investigation reveals that the stability of the double bond in salicylal–glycine



B

is enhanced by complex formation. The method of investigation consisted of a comparison of the spectra of Schiff base complexes of copper(II) with those of the copper complexes of glycine and of salicylaldehyde, and of a continuous variation study of the system copper(II) : salicylaldehyde : glycine.

Experimental

Solution Conditions.—In order to effect the solution of all components of the various mixtures to be studied, a 50% water–dioxane solvent was used throughout. The upper *p*H limit, beyond which precipitation of copper(II) hydroxide occurs, proved to be *p*H 5; spectrophotometric and continuous variation studies were therefore conducted at *p*H 5 and *p*H 3. Adjustment of *p*H was accomplished by means of a Beckman Model H-2 *p*H meter through addition of dilute sodium hydroxide or nitric acid. (The Beckman readings give very nearly the correct *p*H in 50% dioxane solutions.[4]) The ionic strength of the solutions was held constant by the addition of sufficient sodium nitrate for a 1.2 *M* concentration (greater than hundredfold excess over the concentrations of the active components).

Reagents.—The 1,4-dioxane was purified according to the procedure described by Weissberger and Proskauer.[5] Eastman salicylaldehyde was distilled under nitrogen and a heart-cut taken at 196.5°; the product was stored under nitrogen to prevent the formation of oxidation products. Glycine (Merck) was dried for several hours at 110°, and reagent grade copper(II) nitrate (Merck), sodium nitrate (Merck), sodium hydroxide (Baker) and nitric acid (du Pont) were used without purification.

Spectra of the Complexes.—The solutions for the determination of absorption spectra all contained 0.0104 *M* copper(II) nitrate and the calculated quantity of glycine and salicylaldehyde to give the desired concentration ratio in each solution. Plots of the spectra at *p*H 3 and at *p*H 5 are shown in Fig. 1, and in Figs. 2–4, respectively.

Continuous Variation.—The solutions used in the two-component continuous variation experiments all contained copper(II) and glycine or salicylaldehyde at a total concentration of 0.0104 *M*; the ratio of the concentrations of metal ion and organic component, however, varied from solution to solution. The plot of *Y* (observed optical density *vs.* optical density calculated for a system in which no reaction occurs[5a]) *vs.* composition at selected wave lengths is contained in Fig. 5 for copper(II)–salicylaldehyde at *p*H 5 and for copper(II)–glycine at *p*H 3 and 5. Measurements were actually carried out for all solutions at 600, 625, 700, 750 and 768 mμ.

The solutions used for the three-component continuous variation study were made up so that the sum of the concentrations of all three components was 0.0104 *M*. Optical density measurements were made at all of the above wave lengths; *Y*-values at 625 mμ have been plotted for *p*H 3 and *p*H 5 in Figs. 6 and 7, respectively.

Results and Discussion

Spectra at *p*H 3.—Inspection of Fig. 1 reveals that the solution containing two moles of salicylal-

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[1] Presented at the 126th meeting of the American Chemical Society, New York, 1954.

[2] Taken in part from the M.S. thesis of N. Douglas Marchand, Louisiana State University, 1953.

[3] G. L. Eichhorn and J. C. Bailar, Jr., THIS JOURNAL, **75**, 2905 (1953); G. L. Eichhorn and I. M. Trachtenberg, *ibid.*, **76**, 5183 (1954).

[4] M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945).

[5] A. Weissberger and E. Proskauer, "Organic Solvents," Oxford, Clarendon Press, 1935.

[5a] W. C. Vosburgh and S. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

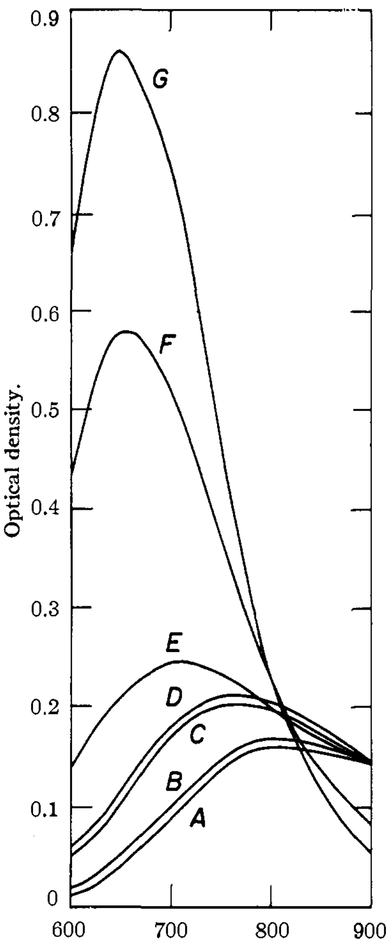


Fig. 1.—Absorption spectra at *p*H 3: A, copper(II) ion; B, 1:2 copper(II)-salicylaldehyde; C, 1:1 copper(II)-glycine; D, 1:2 copper(II)-glycine; E, 1:1:1 copper(II)-salicylaldehyde-glycine; F, 1:2:2 copper(II)-salicylaldehyde-glycine; G, 1:3:3 copper(II)-salicylaldehyde-glycine.

dehyde (B) exhibits virtually the same absorption spectrum as copper(II) itself (A); apparently little or no complex formation takes place between copper and salicylaldehyde. The solution containing one mole of glycine per mole of copper (C) has a more intense peak at a lower wave length, indicating complex formation; addition of a second mole of glycine, however, has little effect on the spectrum (D). The solution containing one mole each of salicylaldehyde and glycine per mole of copper (E) exhibits another increase in absorption and decrease in the wave length of the peak; the presence of two (F) and three (G) moles of both organic constituents per mole of copper effects, respectively, a three- and fourfold increase in extinction over that produced by glycine.

It is significant that salicylaldehyde alone produces virtually no change, and glycine alone produces a small change, in the absorption spectrum of copper(II), but that salicylaldehyde and glycine together bring about a very marked change. These observations suggest that the three-component complex between copper(II), salicylaldehyde and glycine is much more stable at *p*H 3 than the copper complexes of salicylaldehyde and glycine alone. The great difference in extinction coefficient between the two- and three component complexes points to possible analytical applications; thus a solution of copper-glycine might be used for the determination of hydroxyaldehydes, and a solution of copper salicylaldehyde for a determination of amino acids.

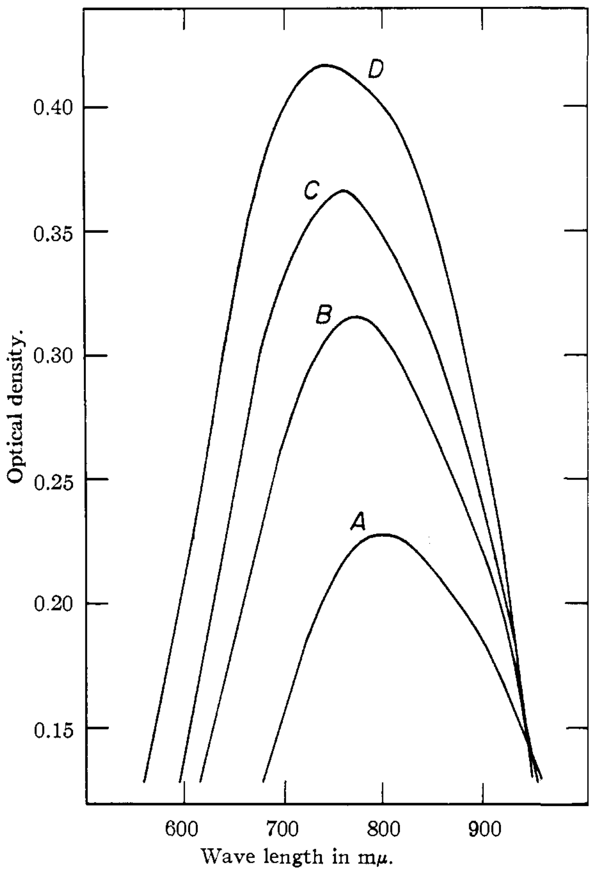


Fig. 2.—Absorption spectra at *p*H 5: A, copper(II) ion; B, 1:1 copper(II)-salicylaldehyde; C, 1:2 copper(II)-salicylaldehyde; D, 1:3 copper(II)-salicylaldehyde.

Spectra at *p*H 5.—The spectra of salicylaldehyde-copper solutions at *p*H 5 (Fig. 2) do differ significantly from those of copper(II), indicating that salicylaldehyde and copper(II) do complex at this *p*H. The copper-glycine solutions at *p*H 5 (Fig. 3) exhibit the usual characteristics of compounds containing copper-nitrogen bonds; the intersection of curves C and D with B points to the presence of two complexes in the solution. At *p*H 5 the spectra of solutions containing all three components (Fig. 4) do not show a large increase in absorption over the solutions of the two-component complexes as at *p*H 3. Since equilibrium at the higher *p*H favors the formation of complex in the copper-glycine system, the presence of the salicylaldehyde does not yield an appreciably greater concentration of complex.

Two-component Continuous Variation.—The wave lengths 600, 625, 700, 750 and 768 mμ were selected for continuous variation studies upon examination of Figs. 1–4. Some significant curves for

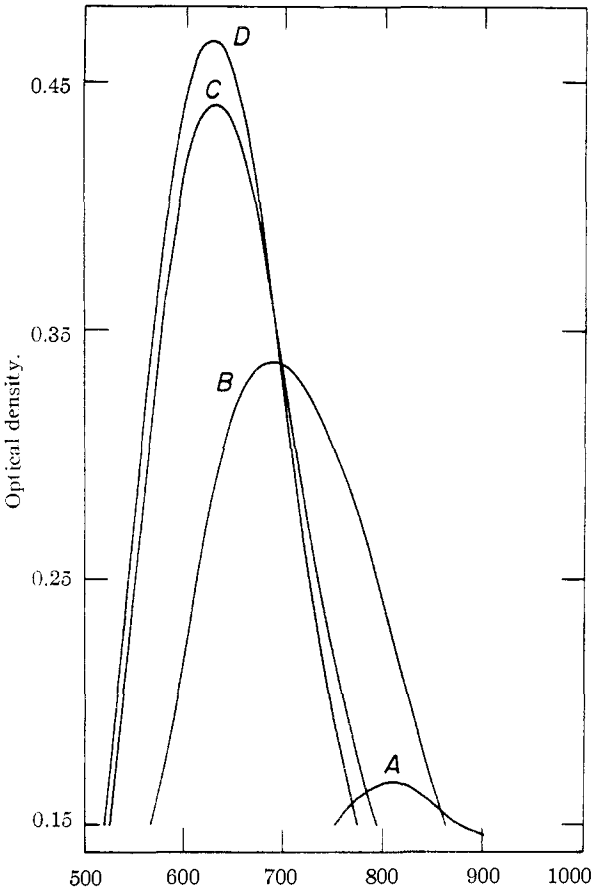


Fig. 3.—Absorption spectra at pH 5: A, copper(II) ion; B, 1:1 copper(II)-glycine; C, 1:2 copper(II)-glycine; D, 1:3 copper(II)-glycine.

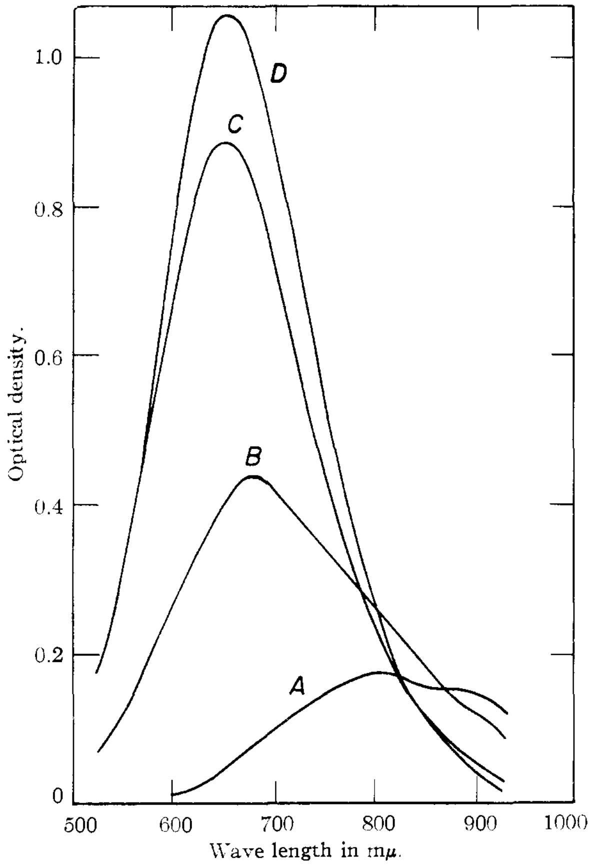


Fig. 4.—Absorption spectra at pH 5: A, copper(II) ions; B, 1:1:1 copper(II)-salicylaldehyde-glycine; C, 1:2:2 copper(II)-salicylaldehyde-glycine; D, 1:3:3 copper(II)-salicylaldehyde-glycine.

the studies on two-component systems are contained in Fig. 5.

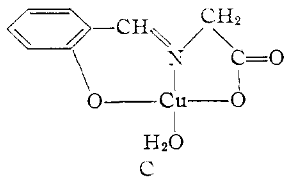
The curves for copper-glycine at pH 3 all pass through a maximum at 50 mole % glycine (Fig. 5a, 750 mμ).[6] Peaks for copper-salicylaldehyde at pH 5 occur at 50 mole % salicylaldehyde (Fig. 5b, 750 mμ). Copper-glycine solutions at pH 5 exhibit maxima at the following compositions:

Wave length, mμ	Mole % glycine
600	66
625	67
700	50
750	45
768	45

The curves for 625 and 700 mμ are reproduced in Fig. 5c and 5d, respectively.

It may be concluded that at pH 3 copper(II) does not complex with salicylaldehyde, and forms a 1:1 complex with glycine. At pH 5 copper(II) forms only a 1:1 complex with salicylaldehyde, and both a 1:1 and a 1:2 complex with glycine.

Three-component Continuous Variation.—Figure 6 represents a plot of constant value Y contours on a three-dimensional composition graph for the three-component continuous variation solutions at pH 3 and 625 mμ. It can be seen that a three-dimensional maximum occurs at a solution composition approximating a 1:1:1 ratio of copper, salicylaldehyde and glycine. Such a maximum would result from the presence of a complex of copper with one mole of the Schiff base



C

The formation of compound C is presumably responsible for the large difference in optical density at pH 3 between the three component and two component complexes. Evidence for the 1:1:1 complex was likewise obtained at all other wave lengths.

A similar Y *vs.* composition plot for pH 5 at 625 mμ is contained in Fig. 7; the peak occurs at a point corresponding to a complex containing two moles of glycine and salicylaldehyde each per mole of copper.[7] This peak can be ascribed to a complex of copper(II) with two moles of Schiff base.[8]

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(6) At 600 and 625 mμ the maxima are at 55 mole % glycine.

(7) There is the suggestion also of the presence of a glycine-rich complex, whose exact composition cannot be determined from the graph. Evidence for the 1:2:2 complex and the glycine-rich complex is contained in plots for the other wave lengths as well.

(8) A coördination number of six for copper(II), involving four strong square coplanar bonds and two weak electrostatic bonds may no longer be considered unusual.

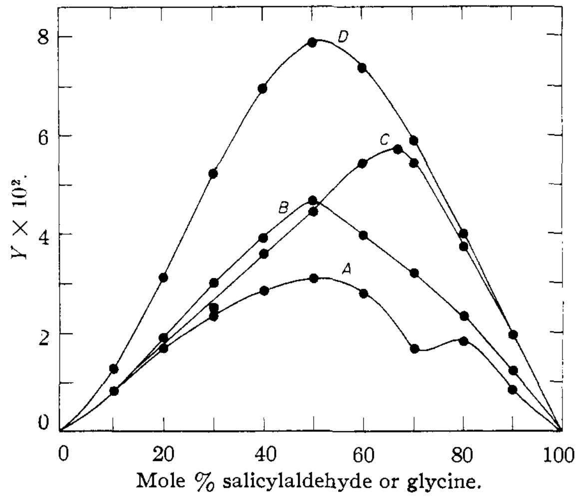
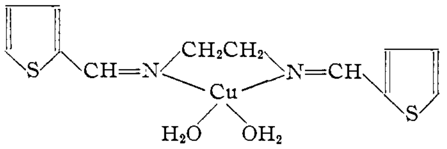


Fig. 5.—Two-component continuous variation: A, copper(II)-glycine, *p*H 3, 750 mμ; B, copper(II)-salicylaldehyde, *p*H 5, 750 mμ; C, copper(II)-glycine, *p*H 5, 625 mμ; D, copper(II)-glycine, *p*H 5, 700 mμ.

Figures 6 and 7 reveal that stable complexes produce maxima at the proper composition ratios in a three-dimensional continuous variation plot in much the same way as in the previously studied two component systems.

The Effect of Metal Ions on Schiff Base Stability.—The coördination of copper(II) with bis-2-thiophenal-ethylenediamine



D

weakens the carbon–nitrogen double bond so that it becomes more readily susceptible to hydrolytic cleavage. The coördination of copper(II) with salicylalglycine (C), on the other hand, stabilizes the double bond to such an extent that the Schiff base complex is capable of existence at *p*H 3, where the uncomplexed Schiff base is dissociated, and the two-component complexes are very unstable.

It has been postulated that the double bond in D is weakened because the copper brings about a reorientation of the electron cloud around the nitrogen in the direction of the copper, and therefore away from the CN double bond. The same effect should also be a factor in labilizing compound C. Why, then, is the double bond strengthened in C and weakened in D?

The answer may be as follows. After the double bond has been severed in D, and the thiophenaldehyde liberated, all of the atoms which were coördinated to copper in D are still coördinated in the resulting ethylenediamine copper complex. Both complexes contain one chelate ring; consequently the electron distortion factor determines the relative stability of the two complexes.

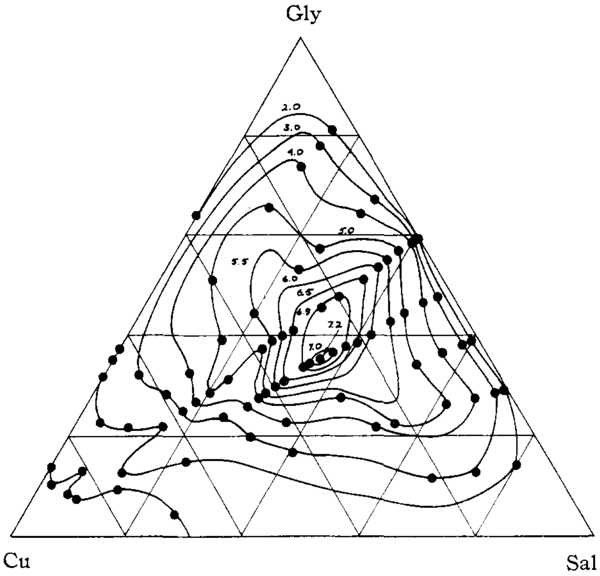


Fig. 6.—Three-component continuous variation, *p*H 3, 625 mμ. Contours are for constant Y-values; numbers are Y × 10².

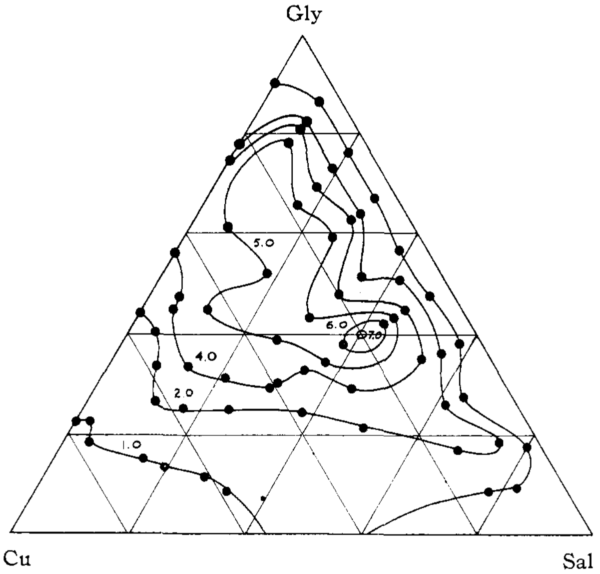


Fig. 7.—Three-component continuous variation, *p*H 5, 625 mμ. Contours are for constant Y-values; numbers are Y × 10².

If the double bond were to be severed in C, on the other hand, causing liberation of the salicylaldehyde, the copper would no longer be coördinated to the oxygen, and the bicyclic chelate ring structure of the Schiff base complex would degenerate into a monocyclic chelate. The difference in stability of the bicyclic and monocyclic structures is apparently more than sufficient to offset the effect of the polarization of the nitrogen atom; consequently a stabilization of the double bond becomes the net result of the action of copper on salicylalglycine.

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