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The Coordinating Tendencies of Some Carboxylic Acids Containing Olefinic Linkages[1]

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In an attempt to extend the range of metals forming stable olefin complexes, a systematic polarographic and potentiometric investigation of the effect of variation of structural features of some unsaturated carboxylic acids on the stability of complexes formed with Cu(II), Cu(I), Ag(I), and Zn(II) was carried out. The carboxylic acids investigated were 2-butene-1,4-dicarboxylic, vinylacetic, crotonic, fumaric, and maleic. Interaction of the olefinic linkage with Cu(I) was found to be considerably greater than for the other metal ions. There was some indication of interaction of Cu(II) with the olefinic linkage, whereas Ag(I) showed surprisingly little tendency to coordinate. No interaction with the olefinic linkage was indicated by the results with Zn(II).

Introduction

A number of metals form stable complexes with olefins, but formation constants are usually lacking. Those metals which form stable olefin complexes, including Cu(I) and Ag(I), occupy an area of more or less triangular shape in the periodic table.[2] The possibility of extending this area was explored in the present work. It was hoped to accomplish this by employing unsaturated ligands containing a carboxylic acid group oriented in such a manner to the double bond as to facilitate chelation to the metal through both the carboxylate ion and the double bond. Several carboxylic acids which contain olefinic linkages previously have been investigated as ligands, but not systematically enough to evaluate the relative importance of the unsaturated linkage and the carboxylic acid group. Keefer, Andrews, and Kepner[3] have studied complexes of CuCl with a variety of unsaturated acids, some of which are included in the present work. Other workers[4-6] have determined the stabilities of complexes of some unsaturated acids. The variation of the structural features of some unsaturated carboxylic acids and the effect on the stability of complexes formed with Cu(II), Cu(I), Ag(I), and Zn(II) are discussed here. The ligands investigated were

$HO_2CCH_2CH{=}CHCH_2CO_2H$

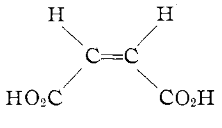
2-Butene-1,4-dicarboxylic acid

$CH_2{=}CHCH_2CO_2H$

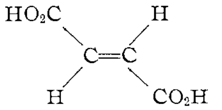
Vinylacetic acid

$CH_3CH{=}CHCO_2H$

Crotonic acid



Maleic acid



Fumaric acid

Experimental

Chemicals.—The 0.01 *M* copper(II) solution was prepared from $Cu(ClO_4)_2 \cdot 6H_2O$, obtained from G. Frederick Smith Chemical Co., and standardized by electrolytic deposition. The 0.01 *M* stock solution of silver nitrate, Fisher Certified, was standardized gravimetrically (as AgCl). The 0.1 *M* sodium hydroxide solution (carbonate-free) was standardized with potassium acid phthalate.

Fisher Certified buffer solution of pH 4.00 was used to standardize the pH meter. Coleman and Bell Co. C.P. sodium nitrate was used in the polarographic investigations.

The vinylacetic acid, obtained from Aldrich Chemical Co., was vacuum distilled; the fraction that distilled at 68° and 10 mm. was collected. In the polarographic investigation, standard 2.438 and 0.970 *M* aqueous stock solutions of the acid were neutralized with sodium hydroxide to give the sodium salt of the acid.

Crotonic acid, Eastman Practical, was recrystallized from petroleum ether (b.p. about 90°) and dried in a vacuum oven. Maleic acid, Eastman Technical, was used without further purification, since the studies with the ligand were not carried beyond preliminary experiments. A stock solution of fumaric acid, Fisher Purified, was standardized with sodium hydroxide.

The 2-butene-1,4-dicarboxylic acid, obtained from K and K Laboratories, Inc., was purified by recrystallization from boiling water and dried at 50–60° in a vacuum oven. The melting point was 194–197°. The acid was standardized by titration with sodium hydroxide and found to be 99.81% pure.

In the polarographic investigation of 2-butene-1,4-dicarboxylic acid, the standard stock solution of the sodium salt was prepared by adding to a weighed amount of the acid enough sodium hydroxide to bring the pH to 6.75. The concentration of the 2-butene-1,4-dicarboxylate ion was determined from the weight of acid used, taking into account the purity of the acid as determined by a previous titration with sodium hydroxide.

It was observed that mold formed in aqueous solutions of 2-butene-1,4-dicarboxylic acid that were left standing for several weeks.

Apparatus and Procedure.—Polarograms were recorded using a Sargent Model XV polarograph. Potentials were measured to the nearest mv. with an external potentiometer.

An H-cell was used which contained a 4% agar-saturated potassium chloride gel and a sintered glass disk to hold the gel in place.

A low resistance Sargent saturated calomel electrode (s.c.e.) was immersed in a saturated KCl solution in one side of the cell, and the dropping mercury electrode (d.m.e.) was placed in the other side, which contained the test solution. The total resistance between the d.m.e. and the s.c.e. was about 570 ohms, and potentials were corrected for the *iR* drop through the cell.

Oxygen was removed from the solution to be analyzed by bub-

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[1] Presented in part at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962. This research was supported by the Atomic Energy Commission, Contract No. At(30-1)-2274.

[2] I. Leden and J. Chatt, *J. Chem. Soc.*, 2936 (1955).

[3] R. M. Keefer, L. J. Andrews, and R. E. Kepner, *J. Am. Chem. Soc.*, **71**, 2381 (1949).

[4] J. M. Peacock and J. C. James, *J. Chem. Soc.*, 2233 (1951).

[5] J. Schubert and A. Lindenbaum, *J. Am. Chem. Soc.*, **74**, 3529 (1952).

[6] S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938).

bling prepurified nitrogen through the solution for about 25 min. All measurements were made at 25 ± 0.1°.

Rohm and Haas Triton X-100 (0.002%) was used as a maximum suppressor.

The solution to be analyzed was prepared by adding the calculated volumes of the standard Cu(II) solution, the standard carboxylic acid solution (as the sodium salt), and Triton X-100 to a 25-ml. or a 50-ml. volumetric flask and diluting to the mark with water.

For the analysis of polarograms, rising sections of waves were obtained manually. The diffusion current (i_d) was measured at -0.5 v. In cases where the polarogram was split into two waves, the separation was usually not great enough to determine accurately the limiting current of the first wave. In order to circumvent this difficulty, the diffusion current for each wave was taken as one-half the total diffusion current at -0.5 v.

Values of the half-wave potential ($E_{1/2}$) were taken from plots of log $(i/i_d - i)$ *vs* $E_{d.e.}$. For this purpose average current data were used.

The slopes of these plots were used as the criterion of reversibility of the electrode reactions, since all evidence indicated that the reduction processes were diffusion controlled.

The characteristics of the capillary used were $m = 1.748$ mg./sec. with no applied potential and $t = 4.654$ sec. at -0.4 v., measured in distilled water at 25° with the mercury column 44.6 cm. high (uncorrected). In a solution of 0.25 *M* vinylacetate and 0.002% Triton X-100 the value of t at -0.4 v. was 4.458 sec.

Potentiometric titrations were carried out in a jacketed beaker through which water, from a constant temperature bath, was circulated. The beaker was covered and continuously flushed with nitrogen during the titration. A Beckman Model G pH meter, equipped with a glass and saturated calomel electrode pair, was used for the pH measurements.

In the determination of the formation constants, 5 or 7 ml. of the metal ion solution, 5 to 10 ml. of the standard carboxylic acid solution, and sufficient distilled water to make the total volume 100 ml. were added to the titration vessel. Prepurified nitrogen was bubbled though the solution for about 15 min. and it was then titrated with standard 0.1 *N* sodium hydroxide (carbonate-free) while maintaining an atmosphere of nitrogen over the solution. All measurements were made at 25 ± 0.1°.

The acid dissociation constants were determined by titration of a certain volume of the carboxylic acid and sufficient distilled water to make the total volume 100 ml. with standard sodium hydroxide in a nitrogen atmosphere at 25 ± 0.1°.

Calculation of Acid Dissociation Constants.—The acid dissociation constants of 2-butene-1,4-dicarboxylic acid and vinylacetic acid were calculated from the potentiometric titration data in the usual manner.[7] The relationships for the dicarboxylic acid were simplified by the assumptions that $[L^{2-}]$ is negligible for data taken well before the first equivalence point and $[H_2L]$ is negligible for data well beyond the first equivalence point.

Calculation of Formulas and Formation Constants.—The polarographic data obtained for the copper complexes with vinylacetate ion and with 2-butene-1,4-dicarboxylate ion have been treated using the well-established relationships presented elsewhere.[8] From this treatment the number of groups coordinated in the Cu(II) complex and in the Cu(I) complex and the formation constants of the complexes were calculated.

For these calculations the $E_{1/2}$ for the reduction of simple copper(I) ion to copper amalgam, a quantity not experimentally obtainable, must be known. For our calculations a value[9] calculated from thermodynamic data, +0.134 v. (*vs.* s.c.e.), was used.

TABLE I

POLAROGRAPHIC DATA FOR THE VINYLACETATE COMPLEXES

Vinylacetate concn., *M*	$E_{1/2}$, volts *vs.* s.c.e. Cu(II) → Cu(I)	$E_{1/2}$, volts *vs.* s.c.e. Cu(I) → Cu(Hg)	Total diffusion current, μa.
0.085[a]	0.108	−0.121	2.54
.096	.113	− .124	6.07
.097	.110	− .129	6.22
.116	.115	− .131	6.38
.136	.112	− .139	6.15
.155	.114	− .142	6.24
.170	.118	− .145	6.06
.191		− .153	5.88
.194	.115	− .152	6.00
.255[a]	.113	− .161	2.43
.340	.120	− .172	5.79
.388	.118	− .180	5.76
.438	.116	− .191	5.88
.488	.118	− .190	5.58
.585	.116	− .199	5.49
.732	.121	− .211	5.31
.829	.118	− .217	5.25
.975	.120	− .224	5.25

[a] Cu concn. 4.176×10^{-4} *M;* in all others Cu concn. 1.044×10^{-3} *M*.

The formation constants were calculated from the potentiometric titration data by the Calvin[10]–Bjerrum[11] method. The formation constants of the complexes of Cu(II) and Ag(I) with 2-butene-1,4-dicarboxylic acid were also calculated by the method of least squares.[12]

In the former method, $\bar{n}$, the average number of anions bound to a metal ion and L, the concentration of ligand anion, can be calculated from (i) the measured pH, (ii) the first and second dissociation constants for the carboxylic acid, expressions for the material balance for (iii) the metal ion and (iv) the carboxylic acid, and (v) the electroneutrality equation. Plots were made of $\bar{n}$ *vs.* $-\log L$, and values of $-\log L$ at $\bar{n} = 0.5$ and 1.5 gave the stepwise formation constants.

Results

In the absence of complexing agents, polarograms of Cu(II) show only a single polarographic wave corresponding to the reduction to the metal amalgam. In the presence of some complexing agents only one wave is observed, but those complexing agents which stabilize Cu(I) give polarograms showing two waves. The two waves correspond to the reduction of Cu(II) to Cu(I) followed by the reduction of Cu(I) to the metal amalgam.

Vinylacetic Acid.—Copper(II) was reduced in two reversible steps in the presence of vinylacetate ion. The $E_{1/2}$ of the first wave was essentially constant while that of the second wave shifted to more negative values as the ligand concentration was increased. The data for the polarography of Cu(II) in vinylacetate solution are given in Table I. The fact that the first reduction wave did not shift with changing concentration of vinylacetate ion indicated that there was no change in the number of coordinated groups on reduction of Cu(II) to Cu(I).

The diffusion current of the total double wave, at a constant Cu(II) concentration, can be seen to decrease

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(7) R. K. Cannan and A. Kibrick, *J. Am. Chem. Soc.*, **60**, 2314 (1938).

(8) J. J. Lingane, *Chem. Rev.*, **29**, 1 (1941).

(9) L. Meites, "Polarographic Techniques," Interscience Publishers, Inc., New York, N. Y., 1955, p. 128.

(10) M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).

(11) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(12) H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 3397 (1953).

Table II

Polarographic Data for the Reduction of 1.22×10^{-3} *M* Cu(II) in the Presence of 2-Butene-1,4-dicarboxylate

2-Butene-1,4-dicarboxylate concn., *M*	Ionic strength	$E_{1/2}$, volts *vs.* s.c.e. Cu(II) → Cu(I)	Cu(I) → Cu(Hg)	Total diffusion current, μa.
0.528	1.59	+0.014	−0.136	5.47
.594	1.78	.014	− .144	5.37
.660	1.98	.013	− .148	5.32
.726	2.18	.013	− .153	5.12
.792	2.38	.013	− .157	4.91
.859	2.58	.009	− .162	4.78
.925	2.77	.011	− .166	4.66
.991	2.97	.010	− .171	4.54
1.123	3.37	.008	− .175	4.18
1.321	3.96	.006	− .183	3.80

with increasing vinylacetate concentration. This effect caused the diffusion current constant to decrease regularly with increasing concentration. The value calculated at 0.25 *M* vinylacetate concentration was 3.12. The diffusion coefficient of the Cu(II)–vinylacetate complex, calculated from the Ilkovic equation, varied from 7×10^{-6} to 5×10^{-6} cm.^{2}/sec.

The plot of $E_{1/2}$ *vs.* log vinylacetate concentration for the Cu(I) reduction consisted of two intersecting straight lines of slope −0.0839 and −0.110 for the concentration ranges 0.08–0.3 and 0.3–0.98 *M*, respectively. The values obtained for the number of groups attached to Cu(I) in these ranges were 1.42 and 1.87. These results were interpreted as indicating that the predominant species present [for both Cu(II) and Cu(I)] in the range 0.08–0.3 *M* were 1:1 complexes, with 2:1 complexes predominating in the ligand concentration range 0.3–0.98 *M*.

The stepwise formation constants calculated for Cu(II) are log $K_1 = 2.27$ and log $K_2 = 0.46$, and for Cu(I) log $K_1 = 5.84$ and log $K_2 = 0.26$.

The formation constants of the complexes of Cu(II) with vinylacetic acid were also determined potentiometrically. The value of log K_1 obtained was 2.42, in reasonable agreement with that obtained polarographically. This value was the average of four determinations in which the ligand:metal ratio was varied from 21:1 to 10:1. All the values were within 0.1 log *K* unit of the average value.

The value of log K_2 was found to be 2.21, which represents a considerable discrepancy from the polarographic value. The potentiometric value is probably the more reliable. Since the constants are small, it is likely that one complex does not predominate over the other to the extent required for the best polarographic results, as was indicated by the nonintegral values for the number of groups coordinated to Cu(I).

No evidence of complex formation between Ag(I) and vinylacetic acid (ligand:metal ratios of 11:1 and 22:1) was detected by the potentiometric method.

Crotonic Acid, Fumaric Acid, and Maleic Acid.—A single polarographic wave was observed for the reduction of Cu(II) in the presence of the sodium salts of crotonic acid, fumaric acid, and maleic acid. The reduction processes were irreversible for crotonic and fumaric acids and reversible (two electrons) for maleic acid.

The $E_{1/2}$ for the polarographic reduction of Cu(II) in the presence of 0.1 to 0.2 *M* crotonate ion was −0.01 v. Polarograms of Cu(II) with 3.0×10^{-2} *M* fumarate ion and with 0.2 *M* maleate ion gave $E_{1/2}$ values of −0.01 and −0.09 v., respectively. The $E_{1/2}$ for the direct reduction of the hydrated Cu(II) ion to the amalgam is +0.018 v. in 0.1 *M* potassium nitrate.[13]

No evidence of complex formation between Ag(I) and fumaric acid was detected by the potentiometric method. The polarographic study of crotonic acid with Cu(II) indicated essentially no complex formation, so Ag(I) was not studied with this ligand.

Maleic acid was not studied with Ag(I) because studies elsewhere[3] with CuCl indicated that the complex formed was less stable than that with fumaric acid and no complex formation with Ag(I) was detected in the latter case.

2-Butene-1,4-dicarboxylic Acid.—Polarograms of Cu(II) in the presence of 0.03 to 0.3 *M* 2-butene-1,4-dicarboxylate ion resulted in a single irreversible wave. Polarograms of Cu(II) in the presence of 0.5 to 1.3 *M* 2-butene-1,4-dicarboxylate ion, however, gave two reversible waves. The $E_{1/2}$ of both waves was shifted to more negative values with an increase in ligand concentration, but the relative shift was greater for the second wave. Data for the polarographic reduction of Cu(II) in 2-butene-1,4-dicarboxylate ion solutions are given in Table II. Plots of $E_{1/2}$ against the logarithm of the 2-butene-1,4-dicarboxylate ion concentration were linear for both reduction waves and the slopes were −0.0207 and −0.118 for the first and second waves, respectively.

As in the case of the vinylacetate complex, the total diffusion current, and thus the diffusion current constant and the diffusion coefficient, were not constant. The diffusion coefficient of the Cu(II)–2-butene-1,4-dicarboxylate complex varied from 4×10^{-6} to 2×10^{-6} cm.^{2} sec. The diffusion coefficient for the vinylacetate complex was double this value, suggesting a larger size for the 2-butene-1,4-dicarboxylate complex.

The $E_{1/2}$ of both waves was found to be dependent on the ionic strength of the solution. An increase in ionic strength caused both waves to be shifted in the positive direction with the relative shift of the first wave about double that of the second wave. Thus it was necessary to take into account the effect on $E_{1/2}$ of increasing the ionic strength caused by the increase in 2-butene-1,4-dicarboxylate ion concentration. This was done by observing the shift in $E_{1/2}$ of a solution of Cu(II) and 0.559 *M* 2-butene-1,4-dicarboxylate ion caused by the presence of increasing quantities of sodium nitrate. These results are shown in Table III.

The correction for the ionic strength effect was applied by correcting the plots of $E_{1/2}$ *vs.* log 2-butene-1,4-dicarboxylate ion concentration for the amount of

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(13) H. F. Holtzclaw, Jr., K. W. R. Johnson, and F. W. Hengeveld, *J. Am. Chem. Soc.*, **74**, 3776 (1952).

shift in $E_{1/2}$ caused by the increase in ionic strength. Since increasing the ionic strength shifts $E_{1/2}$ in the positive direction and increasing the ligand concentration shifts it in the negative direction, the correction is appreciable.

The corrected plots were also linear but of greater slope than the original plots. The values for the slopes were -0.0538 and -0.125 for the first and second waves, respectively. From these slopes values of p and q were calculated, where p is the number of groups coordinated in the Cu(II) complex and q is the number of groups coordinated in the Cu(I) complex. The results were $q = 2.1$ and $(p - q) = 0.9$ (uncorrected values were 2.0 and 0.35, respectively), which indicated the species present were $[\mathrm{Cu^{I}L_2}]^{3-}$ and $[\mathrm{Cu^{II}L_3}]^{4-}$. The over-all formation constants of these species were calculated and found to be $\log \beta_2 = 5.23$ for the Cu(I) complex and $\log \beta_3 = 3.93$ for the Cu(II) complex.

Since the polarography was carried out with the 2-butene-1,4-dicarboxylic acid in its anion form, it was necessary to work at relatively large values of the ionic strength. It is interesting to note that an increase in the ionic strength would cause a decrease in the activity of water and thus presumably a decrease in solvent stabilization of $[\mathrm{Cu^{II}L_3}]^{4-}$ and $[\mathrm{Cu^{I}L_2}]^{3-}$ and an increase in the ease of reduction. That the increase in ionic strength shifts the $E_{1/2}$ to more positive values indicates at least that the trend is in the right direction. For such high ionic strengths one cannot say much about the effect of changes in the activities of the ionic species.

The formation constants of the complexes of Cu(II) and Ag(I) with 2-butene-1,4-dicarboxylic acid (ligand: metal ratios of 10:1 and 5:1) were determined potentiometrically. The constants calculated for Cu(II) are: $\log K_1 = 3.63$, $\log K_2 = 3.09$, and for Ag(I): $\log K_1 = 3.06$ and $\log K_2 = 2.49$.

The rather large value for K_2 relative to K_1 in both cases is surprising in that the species containing two ligand groups would have a doubly negative charge in the case of Cu(II) and a triply negative charge in the case of Ag(I). These charged species would be expected to be considerably less stable than those containing only one ligand group per metal ion.

In view of the unexpectedly large values of K_2 and the rather small ratio of K_1/K_2, which makes questionable the use of the interpolation at half $\bar{n}$ method, the formation constants were also calculated by the least squares method.

The results obtained by the least squares method gave K_2 larger than K_1 for Cu(II) and, for Ag(I), a decrease in the ratio K_1/K_2 from that observed by the first method.

These results appear to be questionable, for when a plot was made, as a check on the mathematical solution, two parallel straight lines resulted, rather than one straight line as expected.

The results obtained by the method of interpolation at half $\bar{n}$ values are probably more reliable.

No evidence of complex formation between Zn(II) and 2-butene-1,4-dicarboxylic acid was found by either polarography or potentiometry. Polarograms of Zn(II) and 0.4 M 2-butene-1,4-dicarboxylate ion gave a single, ill-defined polarographic wave. In the presence of 1.0 M 2-butene-1,4-dicarboxylate ion, Zn(II) gives a well-defined, but irreversible, wave at -1.05 v.

TABLE III

EFFECT OF VARYING IONIC STRENGTH ON THE $E_{1/2}$ OF THE COPPER COMPLEXES OF 2-BUTENE-1,4-DICARBOXYLATE

$NaNO_3$ added, g.[a]	Ionic strength	$E_{1/2}$, volts vs. s.c.e.		Total diffusion current. μa.
		Cu(II) → Cu(I)	Cu(I) → Cu(Hg)	
0	1.68	+0.013	−0.143	5.57
0.553	2.00	.018	− .139	5.34
1.107	2.33	.021	− .138	5.23
1.660	2.65	.022	− .140	5.12
2.214	2.98	.024	− .136	4.93
2.767	3.31	.025	− .137	4.82
3.320	3.63	.028	− .136	4.68
3.874	3.96	.028	− .138	4.55

[a] The weight given is the total weight of $NaNO_3$ added to a solution of 1.22×10^{-3} M Cu(II) and 0.559 M sodium 2-butene-1,4-dicardoxylate for each run.

Discussion

Formation constants and acid dissociation constants obtained in the present investigation and some others which are pertinent to this discussion are summarized in Table IV.

The stabilization of Cu(I) by vinylacetate ion and 2-butene-1,4-dicarboxylate ion can be taken as an indication of interaction between Cu(I) and the double bond. Presumably such interaction does not occur to any great extent for the anions of crotonic, fumaric, and maleic acids. The higher formation constant for the 1:1 Cu(I) complex with vinylacetate ion, compared to that of Cu(II), and the larger value for $\log \beta_2$ of the Cu(I) complex of 2-butene-1,4-dicarboxylate ion, compared to $\log \beta_3$ of the Cu(II) complex, suggest that the olefinic linkage interacts more strongly with Cu(I) than with Cu(II).

The commercially obtained 2-butene-1,4-dicarboxylic acid was found to have a *trans* configuration for the olefinic bond. This was ascertained from its melting point since the *cis* form melts at 122° and the *trans* form at 197°.[14] Atomic models of *trans*-2-butene-1,4-dicarboxylic acid show that, for a *trans* arrangement of the oxygen atoms *about the metal*, the carboxyl groups and the double bond are in favorable positions for bonding to the metal to give two five-membered rings. However, when the oxygen atoms of the carboxyl group of the *trans* acid coordinate *cis to the metal*, the double bond is not in position to coordinate to the metal. The *cis* form of the acid, which was not available for this study, would be even more favorable for coordination through the double bond. For the *cis* acid in both *cis* and *trans* arrangements of the carboxyl groups *about*

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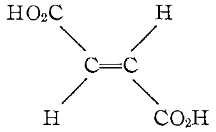
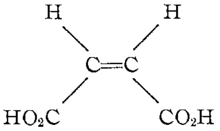
[14] F. Benington and R. D. Morin, *J. Org. Chem.*, **26**, 5210 (1961).

TABLE IV

SUMMARY OF CONSTANTS FOR THE LIGANDS AND COMPLEXES INVESTIGATED[a]

		Acid dissocn. constants		Formation constants							
				Cu(II)			Cu(I)[c]			Ag(I)	
Acid	Structure	pK_{a1}	pK_{a2}	log K_1	log K_2	log β_3	log K_1	log K_2	log β_2	log K_1	log K_2
2-Butene-1,4-dicarboxylic	$HO_2CCH_2CH{=}CHCH_2CO_2H$	3.98	5.00	3.63	3.09	3.93[b]			5.23[b]	3.06	2.49
Vinylacetic	$CH_2{=}CHCH_2CO_2H$	4.37		2.42	2.21		5.84[b] 4.53[3]	0.26	6.10[b]	No complex formation	
Crotonic	$CH_3CH{=}CHCO_2H$	 4.69[d]		No complex formation			One-step reduction 3.20[3]			 −1.04[6]	
Fumaric		3.02[e]	4.39[e]	2.51[4]			One-step reduction 3.96[3]			No complex formation	
Maleic		1.92[e]	6.22[e]	3.90[4]			One-step reduction 3.05[3]				

[a] Constants from earlier work are given on the second line of each row and are indicated by reference numbers. [b] Polarographic results from the present work. [c] The constants given from ref. 3 refer to the complex formed between CuCl and the free acid. [d] J. F. Dippy, *Chem. Rev.*, **25,** 151 (1939). [e] N. E. Topp and C. W. Davies, *J. Chem. Soc.*, 87 (1940).

the metal atom, the double bond is in a favorable position for bonding to the metal.[15]

The larger values of the formation constants of Cu(II) with 2-butene-1,4-dicarboxylic acid as compared to vinylacetic acid and other dicarboxylic acids including glutaric (log K_1 = 3.16), adipic (log K_1 = 3.35), and succinic (log K_1 = 3.33)[4] suggest that interaction between Cu(II) and the double bond occurs in the case of 2-butene-1,4-dicarboxylic acid. The lower value of log β_2 for the Cu(I) complex of 2-butene-1,4-dicarboxylate ion as compared to that of vinylacetate ion is probably the result of the higher charge and the inability of Cu(I) to utilize all six points of attachment of the two ligands in the former complex.

Atomic models of the Ag(I) complex of 2-butene-1,4-dicarboxylic acid indicate that the oxygens of the carboxyl groups could span the metal ion to give a linear arrangement O–Ag–O which is a favorable one for silver. Thus Ag(I) was found to form complexes with 2-butene-1,4-dicarboxylic acid but not with vinylacetic acid, where chelation cannot result in a linear arrangement.

The failure of crotonate ion to show evidence of complex formation with Cu(II) is an indication that the double bond does not contribute to the bonding with Cu(II) to any great extent. No significant stabilization of Cu(I) occurred since Cu(II) was reduced to the metal in one step. Keefer, *et al.*,[3] did obtain an indication of complex formation between the free acid and CuCl. The vinylacetate ion gives complexes with Cu(II) which are only of about the stability to be expected for an acid of this strength. No great interaction with the double bond is indicated. However, the higher pK of crotonic acid would suggest that it should be a better ligand than vinylacetic acid, which was not observed to be the case. Perhaps the double bond does contribute to the stability of the Cu(II)–vinylacetate complex to some extent. The pronounced stabilization of Cu(I) with this ligand indicates that the double bond must be involved in bonding with the metal ion to a great extent. Atomic models bear out that the double bond is in a more favorable position in the vinylacetate ion than in the crotonate ion to permit chelation involving the carboxylate ion and the double bond.

Fumaric acid cannot form a chelate ring with Cu(II) involving both carboxylate ions because of the *trans* configuration. It would be a better ligand than crotonic acid only because of a charge effect resulting from the second carboxylic acid group. The two acids should be almost identical with respect to the opportunity for bonding through the olefinic linkage. Our failure to observe a second polarographic wave for the reduction of Cu(II) in the presence of fumarate ion and the failure to detect any complex formation with Ag(I) and Cu(II) are consistent with the expectation that no appreciable stabilization is brought about by replacing the methyl group by a carboxylate ion on the far side of the molecule or ion. However, other workers[4] have reported a stable Cu(II)–fumarate complex (see Table IV) indicating some enhancement of the complex-forming ability brought about by the replacement of a methyl group by a carboxylate ion. Keefer, *et al.*,[3] found that the complex formed between fumaric acid (not the anion) and CuCl was only slightly more stable than that of crotonic acid. It should be noted that Keefer's results are not inconsistent with our own. If chelation involving the olefinic linkage is not possible, there will be little chance for a metal to bond through the olefinic linkage if a free carboxylate ion is adjacent. The weaker donor properties of the free acid group

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[15] Examination of atomic models is helpful in evaluating the coordinating possibilities of the two alternative ways of coordinating each of the two isomeric acids.

would increase the likelihood of bonding through the double bond.

The acid dissociation constants for maleic acid indicate it is a considerably stronger acid than fumaric acid for the loss of the first proton and a considerably weaker acid for the loss of the second proton. Both of these facts can be explained as the result of the formation of a strong intramolecular hydrogen bond in the monoprotic anion. The formation of a similar chelate ring with Cu(II) causes an increase in the stability of the complex formed relative to that of fumaric acid. However, this chelation would hold the metal ion away from the olefinic linkage. This effect can be noted in the appreciably lower stability of the CuCl complex of maleic acid compared to that of fumaric acid.

The results of this study indicate that there is a considerably greater tendency for bonding through an olefinic linkage for Cu(I) as compared to Cu(II), which is as expected.[2] However, the results also seem to indicate that bonding of Cu(II) through the olefinic linkage occurs in some cases. Silver showed surprisingly little interaction with the olefinic linkage under the conditions of our experiments. However, ligands which are selected because of their ability to form favorable chelate rings in planar, tetrahedral, or octahedral complexes would not necessarily provide the most favorable distribution of the points of attachment for silver ion, which tends to form linear complexes.

Although some indication of interaction of Cu(II) with the olefinic linkage was found, the number of metals which are known to form stable olefinic linkages was not enlarged. In aqueous solution the solvent and the carboxylate ions are probably such strong donors, compared to the olefinic linkage, that olefinic complexes are unlikely except for a few metals.

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Reactions of Triethylaluminum, Diethylaluminum Chloride, and Ethylaluminum Dichloride with Dimethyl-, Trimethyl-, and Tetramethylhydrazines

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Tetramethylhydrazine reacts with triethylaluminum, diethylaluminum chloride, and ethylaluminum dichloride to produce $(C_2H_5)_3Al\cdot N(CH_3)_2N(CH_3)_2$, $(C_2H_5)_2AlCl\cdot N(CH_3)_2N(CH_3)_2$, and $C_2H_5AlCl_2\cdot N(CH_3)_2N(CH_3)_2$, respectively. Nuclear magnetic resonance data indicate that the two nitrogen atoms are equivalent. Molecular weight data indicate that these adducts contain one mole each of the aluminum compound and of the hydrazine per mole of adduct. Therefore, the aluminum atom is probably pentacoordinate in these compounds. The reaction of 1,1-dimethylhydrazine with diethylaluminum chloride produces ethylchloro-2,2-dimethylhydrazinoaluminum, $[C_2H_5AlClNHN(CH_3)_2]_2$. The pyrolytic condensation of ethylchloro-2,2-dimethylhydrazinoaluminum produces the polymer $[AlClNN(CH_3)_2]_x$. The reaction of trimethylhydrazine with ethylaluminum dichloride produces $[Cl_2AlNCH_3N(CH_3)_2]_x$.

Recent studies by Fetter and Bartocha,[1] Laubengayer, *et al.*,[2] Nielsen and Sisler,[3] and Paterson and Onyszchuk[4] have extended the earlier work of Davidson and Brown[5] concerning the reactions of alkylaluminum compounds with Lewis bases. These investigators have shown that alkylaluminum compounds react with amines and hydrazines to produce molecular addition compounds if the Lewis base contains no active hydrogen atoms. If a hydrogen atom is present on the nitrogen the reaction may proceed with the evolution of a hydrocarbon and the formation of a covalent bond between aluminum and nitrogen. The resulting amino- or hydrazinoaluminum compound may condense and form a polymeric species if another hydrogen atom is present on the nitrogen atom and another alkyl group is on the aluminum. Studies in this area have been extended by the synthesis, in our laboratory, of a variety of hydrazinoaluminum compounds, several of which apparently contain pentacoordinate aluminum.

Pentacoordinate aluminum has been proposed by Wiberg[6] and by Ruff and Hawthorne[7] as a result of their experiments with amine complexes of aluminum hydrides. Recently Fetter, *et al.*,[8] have reported a series of complexes formed by reaction of trimethylaluminum and aluminum hydride trimethylamine with a variety of amines and hydrazines, and have used nuclear magnetic resonance spectra to support the postulated existence of pentacoordinate aluminum in these compounds. The existence of pentacoordinate aluminum in solid $AlH_3\cdot 2N(CH_3)_3$ has recently been established by X-ray studies of single crystals.[9]

Before the publication of the above paper[9] we had

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