

cannot be excluded, although we have no evidence for it at this stage.

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Registry No. *cis*- β -(*RR,SS*)-[Cr(ox)(3,2,3-tet)]ClO₄, 81688-76-8; Δ (-)₅₈₉-*cis*- β -(*RR*)-[Cr(ox)(3,2,3-tet)][HBzOT], 81739-55-1; Λ (+)₅₈₉-*cis*- β -(*SS*)-[Cr(ox)(3,2,3-tet)]ClO₄, 81739-53-9; Λ (-)₅₈₉-*cis*- β -(*RR*)-[Cr(ox)(3,2,3-tet)]ClO₄, 81739-56-2; *cis*- β -(*RR,SS*)-[CrCl₂(3,2,3-tet)]ClO₄, 81738-84-3; Δ (-)₅₈₉-*cis*- β -(*RR*)-[CrCl₂(3,2,3-tet)]ClO₄, 81739-51-7; *trans*-(*RR,SS*)-[CrCl₂(3,2,3-tet)]NO₃, 81688-78-0; *trans*-(*RR,SS*)-[CrCl₂(3,2,3-tet)]ClO₄, 81688-79-1; (-)₅₈₉-*trans*-(*RR*)-[CrCl₂(3,2,3-tet)]ClO₄, 53625-78-8; *trans*-(*RR,SS*)-[Cr(NCS)₂(3,2,3-tet)]NCS, 81688-81-5; (-)₅₈₉-*trans*-(*RR*)-[Cr(NCS)₂(3,2,3-tet)][HBzOT], 81738-86-5; Δ (-)₅₈₉-*cis*- β -(*RR*)-[Cr(3,2,3-tet)(OH₂)₂]³⁺, 81739-49-3; *trans*-(*RR*)-[Cr(3,2,3-tet)(OH₂)₂]³⁺, 81739-48-2; *cis*- β -(*RR,SS*)-[CrCl(3,2,3-tet)(OH₂)₂]²⁺, 81688-82-6; *cis*- β -(*RR,SS*)-[Cr(3,2,3-tet)(OH₂)₂]³⁺, 81738-87-6; *cis*- β -(*RR,SS*)-[Cr(OH)₂(3,2,3-tet)]⁺, 81739-47-1; *trans*-(*RR,SS*)-[Cr(3,3,3-tet)(OH₂)₂]³⁺, 81688-29-1; *trans*-(*RR,SS*)-[Cr(OH)₂(3,2,3-tet)]⁺, 81688-30-4; *trans*-(*RR,SS*)-[Cr(OH)(Cl)(3,2,3-tet)]⁺, 81688-31-5.

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Proton Association and Metal Stability Constants of 2-Oxalopropionic, α -Ketobutyric, and Acetoacetic Acids

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The proton association constants for the carboxyl protons of 2-oxalopropionic acid (OPA), acetoacetic acid (AAA), and α -ketobutyric acid (AKBA) were determined potentiometrically, and the dissociation constant of the enolic proton of OPA, H₂L, was determined spectrophotometrically. The metal stability constants of AAA and AKBA were calculated for Zn(II), Al(III), and Cu(II) chelates. In all cases complexes having 1:1 molar ratios of ligand to metal ion were formed, and in the aluminum(III) and copper(II) systems 2:1 complexes were also formed. The stability constants of 1:1 OPA chelates of Zn(II), Al(III), and Cu(II) were determined. In addition to 1:1 complexes of OPA, H₂L, formation of a deprotonated species, MH₂L⁻, was detected for Zn(II) and a 2:1 complex of Al(III), ML₂⁻, was detected. The Cu(II) investigation shows the existence of a deprotonated complex, MH₂L⁻, and of binuclear complexes.

Introduction

Research on the reaction kinetics of α -keto diacids in which the second carboxyl function is located on the β -carbon has been of scientific interest since these substrates are present in biological systems and are subject to enzyme catalysis. The reactions reported to date include spontaneous,²⁻¹⁰ metal-catalyzed,⁷⁻¹⁶ and enzymatic^{17,18} decarboxylation, along with the enolization¹⁹⁻²¹ dehydration^{19,21} and hydration²¹ reactions. The substrates that have undergone examination are oxaloacetic acid (OAA), dimethyloxaloacetic acid (DMOAA), fluorooxaloacetic acid (FOAA), and 2-oxalopropionic acid (3-methyl-2-oxobutanedioic acid, OPA).

Initial studies^{2,3} on the decarboxylation of OPA, the ketonization of the enolic α -ketobutyric acid intermediate, and the enolization of OPA have been carried out in this laboratory. Sakkab and Martell² introduced 2-oxalopropionic acid as a substrate for decarboxylation studies for two reasons. First, the β -protons of OAA in D₂O solutions deuterate while the

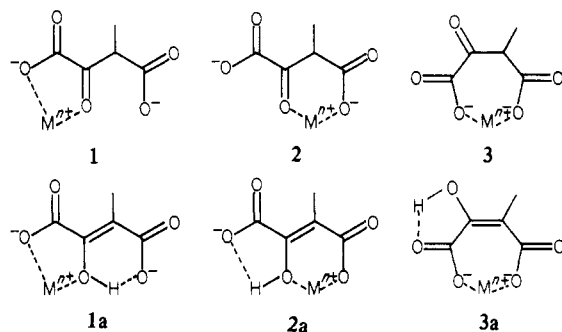
β -methyl group of OPA provides a direct NMR probe during the decarboxylation process, and second, OPA has the ability to enolize and is thus a better model for OAA than DMOAA. The investigation of the metal-catalyzed decarboxylation is the next step in the ongoing work with OPA, which will eventually culminate in the study of pyridoxamine catalysis. The vitamin B₆-catalyzed systems are of importance since the Schiff bases of OAA and its analogues with pyridoxamine are models for the probable intermediates in the corresponding enzyme-catalyzed biological processes.

The first goal of the present investigation is to determine the stability constants of the metal chelates of OPA with Cu(II), Zn(II), and Al(III) so that when kinetics of the corresponding metal-catalyzed decomposition reactions are examined, rate constants for the decarboxylation of the metal chelates may be calculated. The determination of such rate constants makes possible a quantitative description of the effects of metal ions on decarboxylation. Previous potentiometric studies on oxaloacetic acid have reported 1:1 ligand to metal complexes^{12,22-24} along with 2:1 complexes (ML₂)^{22,23} and binuclear chelates (M₂L). Kinetic studies¹¹ of DMOAA inferred the five-membered chelate ring as the active intermediate in decarboxylation with the chelates having six- and seven-membered rings being inactive. Reyes-Zamora and Tsai²⁵ obtained NMR spectra of europium(III) oxaloacetates and concluded that the five-membered ring is preferably formed with no apparent spectral evidence for formation of the larger chelate rings. Covey and Leussing¹⁴ later agreed that the five-membered species of Zn(II) and OAA is the predominant form in their studies but suggested on the basis of thermodynamic principles that 10-20% of the chelate may exist in the seven-membered ring configuration. The second goal of this investigation is to determine if higher order

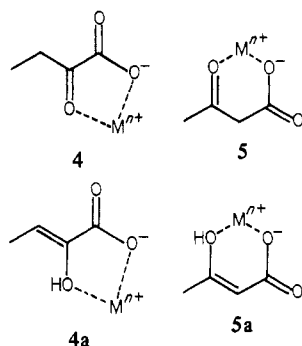
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metal-ligand species (M_2L , ML_2) are present in metal-OPA systems and to elucidate the coordinate bonding of the binary species present as involving any or all of the keto forms 1-3 or enol forms 1a-3a. (In this paper, species with a proton



coordinated to the enolic oxygen are termed "enols", whereas species having a negative (deprotonated) enolic oxygen are called "enolates".) Toward this end, the metal stability constants of α -ketobutyric (AKBA, 4 and 4a) and acetoacetic acids (AAA, 5 and 5a) will also be calculated since they are analogous complexes having five- and six-membered rings, respectively.



Experimental Section

Ligand Synthesis. 2-Oxalopropanoic acid was prepared by acid hydrolysis of diethyl oxalopropanoate, purchased from Aldrich Chemical Co., according to Kubala and Martell.³ α -Ketobutyric acid was obtained from the same source and used immediately. A molecular weight determination revealed further purification to be unnecessary. Ethyl acetoacetate, also purchased from Aldrich Chemical Co., was cleaved by base hydrolysis to acetoacetic acid as described by Krueger.²⁶

Measurements. The pH values were obtained with a Beckman research pH meter fitted either with a Sargent-Welch combination glass electrode or with Fisher calomel reference and universal glass electrodes. The meter was standardized so as to read hydrogen ion concentration directly.

¹H NMR spectra were obtained with a Varian HA-100 NMR spectrometer on 0.8 M OPA solutions, and chemical shifts were reported in parts per million with respect to 3-(trimethylsilyl)propanesulfonic acid, sodium salt. The solvents used were D₂O (99.8% pure), 20% DCl in D₂O (99+%), and 40% NaOD (99+%) and were all obtained from Aldrich Chemical Co. The pD values of the solutions used in the ¹H NMR experiments were calculated by adding 0.40 to the observed reading on the meter.²⁷

Ultraviolet spectra of OPA at a concentration of 1.0×10^{-4} M were taken in the wavelength range from 220 to 350 nm. Throughout the pH range employed, 0.7-13.7, the maximum absorption occurred around 260 nm. The UV spectra were obtained with a Cary 14 recording spectrophotometer in a quartz cell with 1.000-cm path length.

Potentiometric measurements in the absence and presence of metal ions were carried out at 25.00 ± 0.05 °C, and the ionic strength was adjusted to 0.100 by the addition of KCl. The typical ligand concentrations of the experimental solutions were 0.0025 M. For all binary

systems, equilibrium measurements were made on solutions containing 1:1, 1:2, and 1:3 molar ratios of metal ion to ligand. Measurements were discontinued when precipitation became a problem during potentiometric titration. In systems where pH drift resulting from decarboxylation was noticeable, the batch method described by Tate et al.²² was employed. The pH at the time of mixing in these unstable systems was determined by extrapolation of the pH drift to time zero. This method is valid since Leussing et al.^{14,15} have shown the metal (Zn^{2+} , Cu^{2+})-ligand equilibria in these types of systems are very rapid.

Reagents. Stock solutions of reagent grade Al(III), Zn(II), and Cu(II) were prepared from the metal nitrates in doubly distilled water. The exact concentrations were determined by titration with standard EDTA. Al(III) solutions contained excess acid to prevent hydroxide precipitation. This acid was neutralized after the Al(III) and substrate were mixed together. Carbonate-free solutions of 0.100 M KOH were prepared from Dilut-It ampules and standardized with potassium acid phthalate. The supporting electrolyte was potassium chloride, which was obtained as reagent grade material.

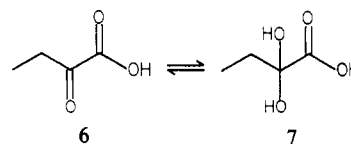
OPA is hygroscopic but is relatively stable toward water vapor when compared to AKBA and AAA. The latter two compounds are extremely hygroscopic and were stored in a desiccator over silica gel in a refrigerator or a cold room (~ 4 °C). Evacuating the desiccator at room temperature can lead to sublimation of both AKBA and AAA. These ligands when in a crystalline form should be handled under dry nitrogen whenever possible to prevent contamination by water.

Computations. Computer programs were developed to calculate values of proton association and metal stability constants. These programs were run on a 64K byte Z-80 microprocessor. The proton association constants for AKBA and AAA were determined with use of the program PKAS.²⁹ The values of the metal stability constants for OPA, AKBA, and AAA were obtained from the BEST³⁰ program, which includes the competition of hydroxide ion for the metal. Values for metal-hydroxide ion stability constants were taken from Martell and Smith.³¹ The difference, σ_{fit} , in the calculated and experimental potentiometric equilibrium curves represents the reliability of the proton association and metal stability constants. When σ_{fit} 's were less than 0.01, the calculated constants were considered to have substantial accuracy. In the reactive systems studied in this work such accuracy is difficult to obtain, but the calculation of proton association and metal stability constants enables one to obtain a more accurate picture of the solution chemistry than that obtained if one had no thermodynamic information at all. The PKAS²⁹ and BEST³⁰ programs were developed by Dr. R. J. Motekaitis.

The proton association equilibrium constant (K_3) for the enolic hydrogen of OPA was calculated from the UV spectra. Extinction coefficients were assigned to all species present. With use of the ultraviolet data obtained in the pH range 11.7-13.7, K_3 was calculated to best fit the data by means of the Newton-Raphson method of iteration.³²

Results and Discussion

Metal-Free AKBA. In the absence of added metal ions, the potentiometric equilibrium curve, shown in Figure 1, is seen to possess a sharp inflection at $a = 1$, where a is moles of base per mole of ligand. Abbott and Martell³³ have shown the keto (6) and hydrate (7) forms of AKBA exist in equilibrium at



pH 4, and the inflection in Figure 1 corresponds to the neutralization of the carboxyl proton. The protonation constant, K_1 , can be defined by eq 1, where [HL] represents the total

$$K_1 = \frac{[HL]}{[L^-][H^+]} \quad (1)$$

concentration of neutral acid, 6 and 7, and $[L^-]$ is the con-

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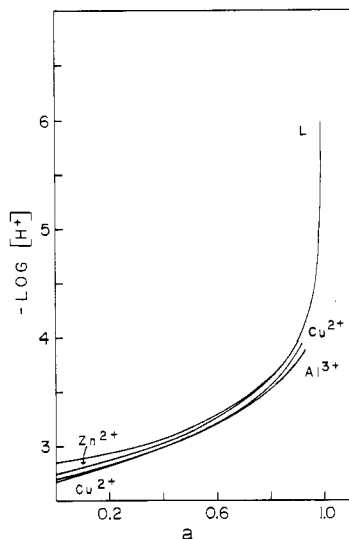


Figure 1. Potentiometric equilibrium curves of a solution containing a 1:1 molar ratio of metal ion to α -ketobutyric acid at 25 °C, $\mu = 0.100$ M (KCl). In each case $[M]_T = [L]_T = 2.5 \times 10^{-3}$ M; a = moles of base added per mole of AKBA.

Table I. Protonation Constants of AKBA, AAA, and Analogous Compounds

	$\log K_1$	σ_{fit}	temp, °C	μ (ionic strength)
AKBA	2.48	0.02	25	0.1
AKBA ³¹	2.50		25	0.0
pyruvic acid ³¹	2.26		25	0.1
butanoic acid ³¹	4.63		25	0.1
acetic acid ³¹	4.56	0.03	25	0.1
AAA	3.57	0.01	25	0.1
AAA ³¹	3.65		18	0.0

centration of the corresponding anion(s). $\log K_1$ can be calculated directly from the potentiometric equilibrium data with a value equal to 2.48 when the experimental conditions are 2.5×10^{-3} M at 25.0 °C and $\mu = 0.10$ M. This value is listed in Table I along with values of analogous compounds.

Metal Ion-AKBA. The potentiometric equilibrium curves in Figure 1 for a 1:1 molar ratio of metal to ligand indicate that Al(III), Zn(II), and Cu(II) interact weakly with AKBA only after substantial dissociation of the carboxyl proton. In Figure 1 the Al(III) curve begins above the Cu(II) curve and finishes below that of the Cu(II) ion. This behavior is attributed to partial hydrolysis of the Al(III), a reaction that was taken into account in the calculations of formation constants. Additional potentiometric data (not shown) were obtained from 1:2 and 1:3 metal to ligand systems. These curves indicate no appreciable formation of 3:1 complexes of Zn(II), Cu(II), and Al(III) and no 2:1 complexes of Zn(II) under the experimental conditions employed (2.5×10^{-3} M AKBA in 0.10 M KCl at 25.0 °C). However, it was found that Al(III) and Cu(II) ML_2 species are present in substantial amounts. The mathematical model that explains the potentiometric data can be summarized in terms of the equilibrium quotients (1), (2), and (3). In the calculation of K_{ML} , a value was assumed

$$K_{ML} = [ML^{(n-1)+}] / [M^{n+}][L^-] \quad (2)$$

$$K_{ML_2} = [ML_2^{(n-2)+}] / [M^{n+}][L^-]^2 \quad (3)$$

for K_{ML_2} , and K_{ML} was calculated from the 1:1 system. This value of K_{ML} was then employed in the calculation of K_{ML_2} . This process was repeated until K_{ML} and K_{ML_2} no longer varied. The overall formation constants and their σ_{fit} are reported in Table II along with metal stability constants of related compounds for comparison.

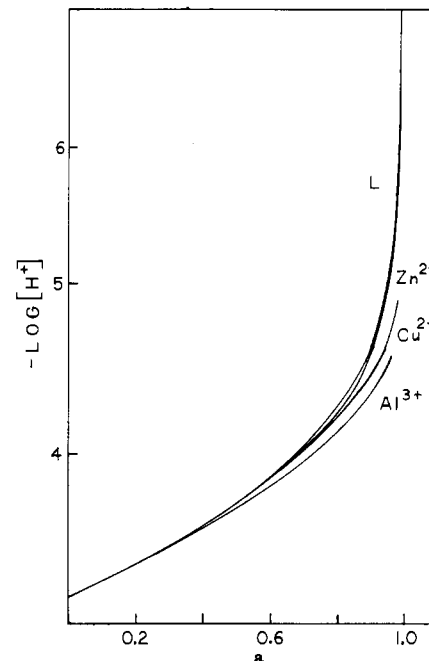
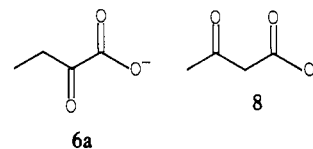


Figure 2. Potentiometric equilibrium curves for acetoacetic acid with Zn(II), Cu(II), and Al(III) at 25.0 °C and $\mu = 0.100$ M (KCl). $[M]_T = [L]_T = 2.5 \times 10^{-3}$ M; a = moles of standard alkali added per mole of AAA present.

It is thought that AKBA is a bidentate ligand and chelates metal ions as shown in structures 4 and 4a. The magnitudes of the metal stability constants suggest that AKBA is bidentate since a noncoordinating carbonyl would reduce electron density on the carboxyl group and lower the stability of its complexes relative to those of butanoic acid. However, the stabilities of AKBA-metal complexes are greater than those of butanoic acid, indicating the carbonyl oxygen is coordinated to the metal ion. It is also noteworthy that the proportion of AKBA in the enolic form would be expected to increase in the presence of metal ions, which tend to stabilize structure 4a by coordination. The higher basicity of the α -hydroxyl substituent results in enhanced stability as evidenced by the greater stability the analogous hydroxy compound, 2-hydroxybutanoic acid, has with metal ions.

Metal-Free AAA. The potentiometric equilibrium curve of AAA in the absence of metal ions is very similar to that of α -ketobutyric acid under the same experimental conditions. In Figure 2 there is a sharp inflection at $a = 1$ with the curve oriented at slightly higher pH values than those observed for AKBA, indicating the weaker acidity of the carboxyl proton of acetoacetic acid. The log of the protonation constant of AAA (eq 1) is calculated as 3.57. The larger value of $\log K_1$ for AAA relative to that for AKBA can be explained on the basis of the structures of the monoanions, 6a and 8. With



the carbonyl adjacent to the carboxyl 6a a conjugated system exists, which helps to stabilize the monoanion by delocalization of the negative charge. Acetoacetate (8), however, does not possess this type of stabilization.

Metal Ion-AAA. The potentiometric data for the 1:1 molar ratio of metal ion to AAA shown in Figure 2 also resemble the AKBA data in Figure 1, with poor metal ion complexation, which weakly perturbs dissociation of the carboxyl proton, the main difference being that interaction of metal ions with AAA is somewhat less. In fact, the presence of Zn(II) has very little

Table II. \log (stability constants)^a of AKBA, AAA, and Related Compounds with Metal Ions at 25.0 °C and $\mu = 0.10$

	$\log K_{ML}^{Zn}$	$\log K_{ML}^{Al}$	$\log K_{ML_2}^{Al}$	$\log K_{ML}^{Cu}$	$\log K_{ML_2}^{Cu}$
2-hydroxybutanoic acid ³¹	1.72			2.66 (0.3) ^b	4.5 (2) ^b
AKBA	1.69 (0.04)	2.09 (0.03)	3.65 (0.03)	2.15 (0.01)	3.99 (0.01)
pyruvic acid ³¹	1.26 ^c			2.2 ^d	4.9 ^d
3-hydroxybutanoic acid ³¹	0.99			1.88 (0.05)	2.9 (0.2)
AAA	0.83 (0.03)	1.21 (0.04)	1.84 (0.04)	1.39 (0.05)	2.37 (0.05)
butanoic acid ³¹	0.98 ^b	1.58		1.7 ^b (0.2)	2.6 (0.2) ^b

^a σ_{fit} values are parentheses after K values for AKBA and AAA; the remaining values in parentheses are errors as reported in the literature. ^b $\mu = 2.0$. ^c $\mu = 0.5$. ^d $\mu = 0.0$.

effect on the dissociation of the ligand. Additional potentiometric work on 2:1 and 3:1 ligand to metal systems, not shown, reveals that Al(III) and Cu(II) form ML_2 species with AAA. The stability constants of these complexes are listed in Table II along with those of the analogous hydroxy compound, 3-hydroxybutanoic acid. The stability constants are smaller than those of 3-hydroxybutanoic acid for the reasons indicated above. It is expected that AAA would form bidentate complexes with metal ions with the keto **5**, and trans-enol, **5a**, monoanions. The results indicate that AAA is a weaker chelating agent than AKBA and that the five-membered chelate ring is more stable than the six-membered ring. Another interesting observation is that butanoic acid forms more stable metal ion complexes than does acetoacetic acid. There are several possible reasons for this, the main one being the inductive effect of the carbonyl in **5**, which removes electron density from the negatively charged carboxyl. Another factor may be that the conjugated system in **5a** delocalizes part of the negative charge of the carboxyl group. Both of these factors result in a weakening of the coordinating tendency of the carboxylate group. Another consideration is the possible existence of the monodentate cis enol. However, it is believed that this is not a major factor.

Metal-Free OPA. Figure 3 shows the potentiometric equilibrium curve of 3.33×10^{-3} M OPA titrated with 0.0101 M KOH. There is a slight break at $a = 1$ and a very sharp inflection at $a = 2$, corresponding to the deprotonation of the two carboxyls. The proton equilibria are shown in Scheme I, and the related proton association constants are defined by eq 5 and 6. Previous studies³ have shown $\log K_1$ and $\log K_2$

$$K_H = [\text{keto } \mathbf{10}] / [\text{hydrate } \mathbf{9}] \quad (4)$$

$$K_1 = [H_2L] / [HL^-][H^+] \quad (5)$$

$$K_2 = [HL^-] / [L^-][H^+] \quad (6)$$

$$K_E = [\text{keto } \mathbf{12}] / [\text{enol } \mathbf{13}] \quad (7)$$

$$K_3 = [L^{2-}] / [H_2L^{3-}][H^+] \quad (8)$$

to be 1.75 and 4.18, respectively. The proton association, K_3 , of the enolate, **14**, to the enol, **13**, as shown in Scheme I and defined by eq 8 cannot be calculated accurately from potentiometric data since the enolate species is never greater than 1% under the experimental conditions employed. As a consequence of this, it was necessary to determine the value of K_3 spectrophotometrically.

Figure 4 is a plot of the absorbance at 260 nm of a 1.0×10^{-4} M solution of 2-oxalopropionic acid ($\mu = 0.1$ M KCl, $t = 25.0$ °C) as a function of pH. The pH dependence of the optical density of OPA is similar to that observed for the analogous compound oxaloacetic acid.^{9,20} The increase in absorption that accompanies an increase in pH is due to the hydrogen ion dependence of the hydrate-keto-enol equilibrium pictured in Scheme I. Hydration at the carbonyl is facilitated by the protonation of the adjacent carboxyl group,³⁴ resulting in significant amounts of hydrate species, **9**, at low pH. The enol tautomer increases in concentration upon ionization of

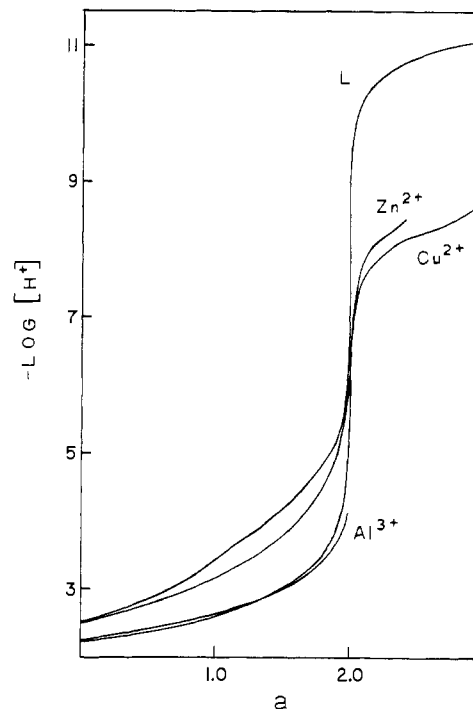
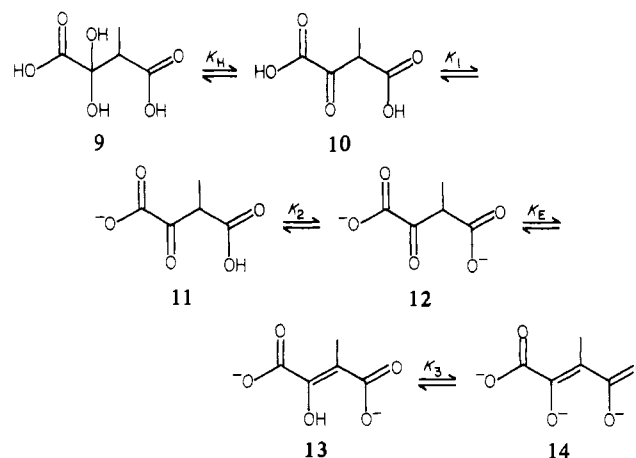


Figure 3. Potentiometric equilibrium curves of a 1:1 molar ratio of metal ion to oxalopropionic acid at 25.0 °C and $\mu = 0.100$ M (KCl). $[M]_T = [L]_T = 3.33 \times 10^{-3}$ M; a = moles of base added per mole of OPA. The curves are composites of measurements made on many solutions to avoid interference by decarboxylation.

Scheme I



the carboxyl groups because of the fact that enolization of the keto dianion, **12**, to the enol dianion, **13**, subsequently results in conjugation, which in turn stabilizes the negative charge. This interpretation of the ultraviolet data is supported by the ¹H NMR spectra listed in Table III. At pD 2.47 the hydrate resonance appears 1.10 ppm downfield from Me₄Si with the keto signal at 1.14 ppm. When pD is increased to 8.35, the hydrate signal is no longer present while the keto signal shifts slightly upfield with the enol resonance located at 1.33 ppm.

The ionic strength is not adequately controlled by 0.10 M

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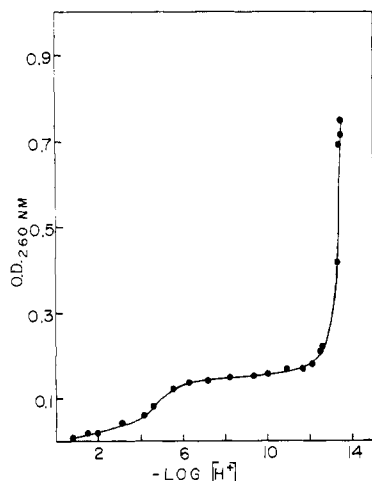


Figure 4. Optical density at 260 nm of a 1.0×10^{-4} M aqueous solution of 2-oxalopropionic acid at 25.0 °C with the 0.100 M ionic strength controlled by the addition of KCl.

KCl above pH 12. Since ionic strength affects the value of the proton association constant, it was necessary to plot absorbance vs. ionic strength and extrapolate back to $\mu = 0.10$ at each pH value above 12. These calculated absorbances are employed in Figure 4.

The extinction coefficient, ϵ_{14} , for the enolate, **14**, was determined by measuring the absorbance of several solutions of OPA in 10 M KOH. The spectra were obtained immediately after mixing in order to prevent impurities due to aldol condensation from interfering with the absorbance measurements. The concentration of OPA varied from 0.98×10^{-5} to 5.4×10^{-5} M, and ϵ_{14} was calculated from the slope of a plot of absorbance vs. concentration. The value of the extinction coefficient of the enolate species was found to be 24.6×10^3 $M^{-1} \text{ cm}^{-1}$.

Below pH 5 NMR shows that the hydrate, **9**, and keto neutral acid, **10**, keto monoanion, **11**, and keto dianion, **12**, are the major forms of OPA. It is assumed that species **9** and **10** do not contribute to the absorbance when the total concentration of OPA is 1.0×10^{-4} M because of their very small extinction coefficients. (Kokesh³⁵ has substantiated a similar assumption, $\epsilon_{\text{hydrate}} + \epsilon_{\text{keto}} \ll \epsilon_{\text{enol}}$.) By the use of eq 4–6 and eq 9 and 10, where A_i is the absorbance of an individual species

$$\sum_{i=1}^n A_i = A_T \quad (9)$$

$$\sum_{i=1}^n [L]_i = [L]_T \quad (10)$$

species present at concentration $[L]_i$ and A_T and $[L]_T$ are total absorbance and total OPA analytical concentration, respectively, the extinction coefficients for **11** and **12** may be calculated by obtaining values for ϵ_{11} and ϵ_{12} that best fit the optical density data. This calculation yields values of 88 and $360 \text{ M}^{-1} \text{ cm}^{-1}$ for ϵ_{11} and ϵ_{12} , respectively.

Between pH 8.35 and 10.33 the percent of enol, **13**, and keto, **12**, forms remains fairly constant with nuclear magnetic resonance data revealing the existence of 5.5% enol dianion and 94.5% keto dianion. With this information, the value of ϵ_{12} , and eq 7 and 9, the extinction coefficient for the enol dianion, ϵ_{13} , can be calculated. The value for ϵ_{13} is $14.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

In the pH range 11.7–13.7, OPA exists in the form of the keto dianion, **12**, the enol dianion, **13**, and the enolate trianion,

Table III. ^1H NMR Determinations^a of Hydrate, Keto, and Enol Species in 0.80 M OPA Deuterium Oxide Solutions^b

pD ^c	% hydrate	% enol	% keto	K_H	K_E
1.55	45		55	1.2	
1.59	40		60	1.5	
1.87	33		67	2.0	
2.94	24		76	3.2	
2.47	16		84	3.2	
2.61	8		92	11.5	
2.76	5		85	19.0	
3.08			100		
3.53			100		
3.94			100		
4.22			100		
4.58			100		
4.83			100		
8.35		5	95		19
8.35		6	94		16
8.92		5	95		19
8.92		6	94		16
9.24		5	95		19
9.24		5	95		19
9.67		6	94		16
9.67		6	94		16
10.33		6	94		16
10.33		5	95		19

^a The absence of values indicates only that these species were not detectable by NMR at this concentration of substrate. The possibility exists that they may be present in quantities of several percent or less. ^b pDs 1.55–4.83 from Kubala and Martell.³ ^c 30 °C, $\mu = 0.10$ M KCl.

14. The two dependent equilibria, enol \rightleftharpoons keto and enol \rightleftharpoons enolate, which relate these three species, are expressed by eq 7 and 8. The enolic proton association constant, K_3 , can now be calculated from the ultraviolet data in this pH region since an average value of K_E may be obtained from Table III. The combination of eq 7–9 gives eq 11. The concentration of enol

$$0 = \epsilon_{12}K_E c_{13} + \epsilon_{13}c_{13} + \frac{\epsilon_{14}c_{13}}{K_3[H^+]} - \frac{A_T}{l} \quad (11)$$

dianion, c_{13} , can be evaluated by using eq 7, 8, and 10 to give

$$c_{13} = \frac{[L]_T - K_3 - [H^+]}{K_E K_3 [H^+] + K_3 [H^+] + 1}$$

Substitution of this expression into eq 11 gives

$$F(K_3) = 0 = K_3[L]_T[H^+](\epsilon_{12}K_E + \epsilon_{13}) - K_3 A_T [H^+](K_E + 1)/l + \epsilon_{14}[L]_T - A_T/l \quad (12)$$

Equation 12 is in the proper form for an iterative solution using the Newton–Raphson³² method, whereby $F'(K_3)$ is the first derivative of $F(K_3)$. K_3 can be solved for data point in the specified pH range. $\log K_3$ determined in this manner was found to be 13.05 ± 0.05 :

$$K_3^{\text{new}} = K_3^{\text{old}} - F(K_3)/F'(K_3) \quad (13)$$

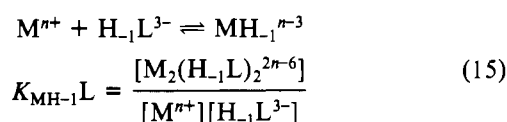
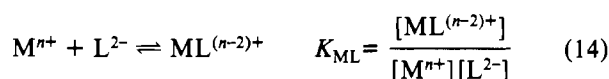
For comparison, the $\log K_3$ value of oxaloacetic acid is 13.03 at 25.0 °C.²² The change in the aqueous medium from acidic to basic may affect the calculated extinction coefficients, which would result in an unreliable value of $\log K_3$. Solvent dependencies are likely for $n - p^*$ transitions but occur infrequently for $\pi - \pi^*$ transitions.³⁶ It is assumed that the ab-

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sorbance at 260 nm for OPA is a $\pi-\pi^*$ transition and solvent independent. This assumption is supported by the relatively small error in the $\log K_3$ value.

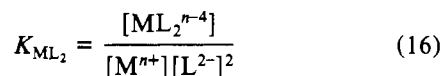
Metal Ion-OPA. Stability constants for OPA-metal ion systems were calculated from the potentiometric curves shown in Figure 3 for systems having a 1:1 ratio of metal to ligand for Al(III), Zn(II), and Cu(II). Measurements for the 2:1 ligand-metal systems were made but are not shown. There is a sharp inflection for Zn(II) at $a = 2$, which indicates that the 1:1 metal-ligand complexes (ML) form only after considerably dissociation of the carboxyl protons. The free-ligand curve is depressed between $a = 2$ and $a = 3$ in the presence of zinc ion because of the formation of an OPA enolate-zinc(II) complex ($MH_{-1}L$). There is no evidence of a 2:1 complex at any point in the potentiometric experiment. The stability constants for the formation of the ML and $MH_{-1}L$ species are defined by the eq 14 and 15, and the values of \log



K_{ML} and $\log K_{MH_{-1}L}$ obtained are listed in Table IV. Pederson⁸ and Gelles and Salama¹² reported the formation of monoprotonated species of metal complexes of oxaloacetic acid, while Covey and Leussing¹⁴ did not observe such species for OAA, which is in agreement with the present study. Gelles and Salama¹² also reported the formation of binuclear complexes in OAA-metal ion systems but Covey and Leussing¹⁴ later showed that such complexes become significant only when there is a large excess of free metal present in solution. No binuclear species were detected for the OPA-metal ion systems in this work.

Tate et al.²² reported a $M(H_{-1}L)_2$ species for Mg^{2+} -OAA systems, but this type of complex was not detected in the present investigation. This observation may be the result of the reaction conditions. Tate et al.²² used magnesium ion and ligand concentrations of 2.5×10^{-2} M, which is a 10-fold excess over the concentrations used in this study.

Analysis of the Al(III)-OPA system was somewhat limited because of aluminum hydroxide precipitation. Evidence was found for the presence of aluminum ML and ML_2 species, but complexes of the MHL, M_2L , and $MH_{-1}L$ type were not observed. The stability constant for the formation of 2:1 complexes is defined by the equation



The values of $\log K_{ML}$ and $\log K_{ML_2}$ for Al(III) listed in Table IV were calculated by the method described above for AKBA-metal ion stability constants.

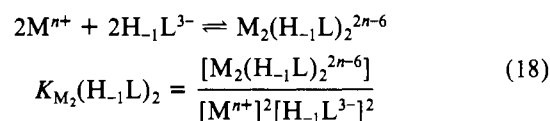
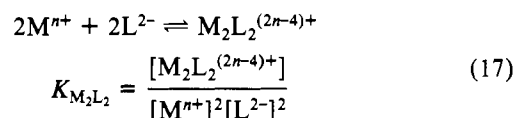
The copper(II) equilibrium curve also has a sharp inflection at $a = 2$, indicating the formation of the ML type complex species. The depression of the free-ligand curve from $a = 2$ to $a = 3$ is indicative of the formation of the $MH_{-1}L$ species. The Cu(II)-OPA system shows no sign of the formation of M_2L , ML_2 , or $M(H_{-1}L)_2$ species, but the magnitudes of K_{ML} and $K_{MH_{-1}L}$ vary with change in concentration of the metal. On the basis of the concentration dependence of the equilibrium constants, it is proposed that dimerization occurs and M_2L_2 and $M_2(H_{-1}L)_2$ complexes exist in Cu(II)-OPA systems.

Table IV. \log (stability constants)^a for Chelate Species Present in OPA-Metal Ion Systems at 25.0 °C in 0.1 M KCl

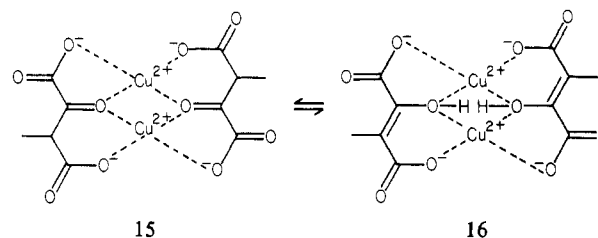
	Cu(II)	Al(III)	Zn(II)
$\log K_{ML}$	5.83 (0.06)	6.16 (0.07)	3.13 (0.04)
$\log K_{ML_2}$		10.80 (0.05)	
$\log K_{MH_{-1}L}$	9.6 (0.1)		7.4 (0.1)
$\log K_{M_2L_2}$	15.5 (0.05)		
$\log K_{M_2(H_{-1}L)_2}$	22.4 (0.1)		

^a Error recorded in parentheses after values.

Equations 17 and 18 give the equilibria and the equilibrium quotients associated with these reactions.



The values of $\log K_{ML}$, $\log K_{MH_{-1}L}$, $\log K_{M_2L_2}$, and $\log K_{M_2(H_{-1}L)_2}$ complexes are presented in Table IV. The dimer stability constants were calculated by an iterative method identical with the one described for the calculation of K_{ML_2} . Possible structures of the M_2L_2 dimers, **15** and **16**, may ac-



count for the ease with which Cu(II) displaces the enolic protons and increases the degree of formation of the enolate species. This type of copper(II) dimer has been suggested for the oxaloacetate-Cu(II) binuclear chelate by Raghavan and Leussing¹⁵ and for malate- and tartrate-Cu(II) binuclear chelates by Rajan and Martell.³⁷

Considerable effort has been spent to ascertain the nature of the metal chelates of oxaloacetate. The current elucidation of the binary OPA-metal chelate structures should support and extend the existing knowledge of the structures of these types of chelate complexes. Six-coordinate bonding arrangements are possible for the chelates formed without dissociation of the enol; two are five-membered rings (**1**, **1a**), two are six-membered rings (**2**, **2a**), and two are seven-membered rings (**3**, **3a**). For OPA it is reasonable to expect that the five-membered ring is favored since the five-membered ring of AKBA is between 0.76 (Cu²⁺) and 0.87 (Al³⁺) log unit more stable than the six-membered chelate ring of AAA. It should be noted that the presence of the second carboxylate group in the basic AAA and AKBA structures should enhance the stabilities of the corresponding metal complexes. For the six-membered chelate ring, **2**, the second carboxylate adds negative charge to the carbonyl through delocalization, which would enhance coordination, while the second carboxylate in the five-membered ring, **1a**, increases the percent of enol dianion in solution since enolization results in conjugation throughout the entire molecule, which better stabilizes the double negative charge. The subsequent increase of the enol species therefore enhances the stabilities of the metal complexes formed since hydroxyl groups coordinate better than

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carbonyls. If the difference between the internal five- and six-membered rings of OPA is approximated to be 0.75 log unit, this means that 15% of the chelate would have a six-membered ring structure and 85% would have the five-membered ring structure.

Proton NMR measurements²⁵ using Eu(III) in unspecified concentrations have shown that oxaloacetic acid complexes of the ML^+ type preferably form five-membered chelate rings. The half-life of Eu^{3+} -OAA chelates should be slightly under 3 min on the basis of values obtained for La(III) and Gd(III).³⁴ Solutions having 1:1 molar ratios of ligand to metal ion at concentrations high enough for the observation of NMR resonances of metal chelates have significant concentrations of the chelates and therefore exhibit considerable catalytic activity. The time required to obtain an initial NMR measurement of the Eu(III)-OAA system is close to the half-life of decarboxylation of the complex. The fact that neither the existence of the hydrate species³⁵ nor the increase in the amount of enol species in solution in the presence of metal ions^{14,15,22} is detected casts some doubt upon the conclusions made in the earlier NMR study. Given a 10% error under these conditions as well as the fact that half the substrate has already decomposed, it appears that initially there may be as much as 20% of an undetected species. Covey and Leussing¹⁴ in their work with OAA came to the same conclusion and suggested the seven-membered ring instead of the six-membered ring to account for the high stabilities of OAA complexes compared to those of pyruvate. This is in accord with the stability of the seven-membered chelate ring of the zinc(II)-succinate complex ($10^{1.76}$).³⁴ Their explanation does not consider the adverse inductive effect on the stability constant resulting from a carbonyl adjacent to one of the carboxylates (3). It is thought the inductive effect is sizable since an adjacent carbonyl has a large effect on the pK_a of the carboxyl.

The difference in the pK_a s of propanoic (4.67)³¹ and pyruvic acids (2.23)³¹ at 25 °C and 0.10 M ionic strength is 2.41 log units while the change in the proton association constants of butanoic (4.63)³¹ and α -ketobutyric acids (2.48) is 2.15 log units. On this basis it is estimated the stability constants of Zn(II)-OAA²⁻ and Zn(II)-OPA²⁻ seven-membered chelates have values well under 10. However, it is believed the log (stability constant) of the six-membered Zn(II)-OPA²⁻ chelate (2) is well over 1 log unit. It may be argued that the OPA cis-enol seven-membered ring, 3a, adds to the stability of the seven-membered chelate, but this is doubtful. A CPK molecular model of this species, 3a, indicates the negatively charged oxygens of both carboxylates come in close contact with each other, resulting in instability because of electrostatic repulsions. The model also demonstrates there is no available space that a metal ion could occupy to stabilize the negative charges on the carboxylates. Also, it is not reasonable to expect the molecule to bend or twist to accommodate a metal ion because of the planarity of the conjugated system and the existence of a hydrogen bond between the hydroxyl and the carbonyl of the adjacent carboxylate. For the reasons stated it is proposed that the five-membered ring is the major chelate species and the six-membered ring is the minor chelate species in OPA- and OAA-metal ion systems, with the seven-membered ring making little or no significant contribution to the solution chemistry.

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Registry No. OPA, 642-93-3; AAA, 541-50-4; AKBA, 600-18-0; Zn, 7440-66-6; Al, 7429-90-5; Cu, 7440-50-8.

Contribution from the Sonderforschungsbereich 127 der DFG (Kristallstruktur und chemische Bindung) and Fachbereich Chemie, Universität Marburg, 3550 Marburg, West Germany

High-Spin-Low-Spin Equilibria of Cobalt(2+) in the Terpyridine Complexes $Co(terpy)_2X_2 \cdot nH_2O$

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For the complexes $Co(terpy)_2X_2 \cdot nH_2O$ with $X = Cl^-, Br^-, I^-, NO_3^-,$ or ClO_4^- and different n values optical spectra, EPR resonances, and magnetic moments are measured between 300 and 4.2 K. From the temperature variation of the susceptibility for different X an equilibrium between the octahedral high-spin 4T_1 and low-spin 2E states of the d^7 configuration can be deduced. The ligand field spectra show nearly exclusively doublet-doublet transitions independent of the high-spin/low-spin ratio. At low temperature EPR spectra of both spin states are observed side by side for $X = ClO_4^-$ and are attributed to differently distorted Co^{2+} sites in the lattice. While the high-spin state seems to be stabilized by the "ligand effect" in combination with spin-orbit coupling, the low-spin g tensors indicate the presence of an additional, rather strong Jahn-Teller distortion. The "ligand effect" corresponds to a tetragonal compression of the CoN_6 octahedra as the consequence of the rigid structure of the terpyridine molecule. In the case of a low-spin ground state this distortion is superimposed by an elongation perpendicular to the direction of compression, which is induced by the Jahn-Teller effect. The low-spin ground state is stabilized with respect to the high-spin ground state by a strong vibronic Jahn-Teller coupling in the octahedral 2E level. The spin exchange can be explained alternatively by an intermolecular, cooperative mechanism as well as by an intramolecular thermal spin equilibrium. The available structural, spectroscopic, and magnetic data are interpreted on the basis of the AO model, with use of the local and cooperative Jahn-Teller effect.

Introduction

The terpyridine complexes of transition-metal ions $T^{II}(terpy)_2X_2 \cdot nH_2O$ crystallize in tetragonal and triclinic structures, depending on the nature of the anion X and the water content n .¹⁻⁴ The two rigid tridentate ligands force upon the

d^n cation a distorted octahedral coordination of approximate D_{2d} symmetry, the dominant characteristic of which is a

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