TABLE I (*Continued*)

| Analyses, % Chlorine Found | Chlorine Calcd. | Carbon Found | Carbon Calcd. | Nitrogen Found | Nitrogen Calcd. | Solubility of lake | Yield, % | Magnetic susc. (Bohr magnetons) | Oxidation state of cobalt |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 10.5 | 10.5 | Sol. in alcohol<br>Insol. in water | 30 | Diamagnetic | +3 |
| | | 69.2 | | | | Sol. in alcohol<br>Insol. in water | 2.1 g. from 3 g. dye | Diamagnetic | +3 |
| | | 51.6 | 51.2 | 4.9 | 4.6 | Insol. in $H_2O$<br>Insol. in 95% alc. | Air-17<br>$N_2$-48 | 5.1(35.2 × $10^{-6}$ units/gm.)<br>4.9(33.1 × $10^{-6}$ units/gm.) | +2 |
| 13.1 | 13.3 | 59.6 | 58.6 | 6.1 | 5.3 | Sol. in 95% alc.<br>Insol. in water | Air-33<br>$N_2$-21 | (1.05 × $10^{6}$ units/gm.)<br>(1.29 × $10^{-6}$ units/gm.) | +3 |
| | | 52.6 | 51.7 | 8.9 | 9.3 | Mod. sol. in acetone and abs. alc. Gives yellow-brown coloration to $H_2O$ | 66 | Diamagnetic | +3 |
| 8.2 (ionic) | 8.0 (ionic) | 45.7 | 46.1 | 4.8 | 4.7 | Easily sol. in water and alcohol. Insol. in benzene and ether | 31 | Diamagnetic | +3 |
| | | | | | | Same as V | 62 | Diamagnetic | +3 |
| | | 52.1 | 51.7 | 9.2 | 9.3 | Same as V and VII | 43 | Diamagnetic | +3 |
| 11.4 | 11.9 | 52.4 | 52.4 | 7.8 | 7.8 | Mod. sol. in acetone and abs. alc. Gives yellow-brown color to $H_2O$ | 67 | | |
| 11.3 | 11.4 | 50.6 | 50.3 | 2.9 | 2.6 | Sl. sol. in abs. alc. Insol. in water | 86 | | |
| | | | | | | Same as X | 65 | | |

lated as $[\mathrm{Coen_2Cl_2}]$ $[\mathrm{Codye_2}]$. (Found: Co, 14.2; C, 44.8. The proposed structure requires Co, 14.75; C, 45.1.)

It was not possible to obtain the cation $[\mathrm{Co(NH_3)_3}$ dye$]^+$ in soluble form because of the ease with which the ammonia molecules are displaced to form the anion $[\mathrm{Co\ dye_2}]^-$. However, a water soluble compound [Co(diethylenetriamine) (dye)]Cl was prepared from the same dye and bisdiethylenetriamine cobaltic chloride. Each molecule satisfies three coördination positions, and the three primary valences of the metal are taken up by the bifunctional dye molecule and the ionic chlorine. The equivalent conductance, measured at a dilution of 1 mole in 1024 liters, indicates that this water-soluble material gives two ions in solution.

With divalent zinc and diortho substituted azomethine dye, 2′-hydroxy-benzal-2-hydroxy-5-chloroaniline, a 1:1 dye:metal lake was obtained. Both primary valences of the metal atom are satisfied by one dye molecule. Higher yields were obtained when the solution was buffered with acetate ion.

The authors take pleasure in acknowledging their indebtedness to the General Aniline and Film Corporation and to the E. I. du Pont de Nemours and Company for grants which made this work possible.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

# Stability of Metal Chelates. III. Iminopropionic-acetic and Aspartic Acids

BY S. CHABEREK, JR.,[1] AND A. E. MARTELL

RECEIVED MAY 12, 1952

The acid dissociation constants of iminopropionic-acetic and aspartic acids, and the first and second chelate stability constants of the corresponding anions with $Co^{+2}$, $Ni^{+2}$, $Cu^{+2}$, $Zn^{+2}$ and $Cd^{+2}$ ions are reported. Comparisons are made with the stabilities of analogous compounds, iminodiacetic and iminodipropionic acids, and the trends observed are interpreted in the light of the probable structures of these chelate compounds.

The stability constants of some transition metal chelates of iminodiacetic (IMDA) and iminodipropionic (IMDP) acids have been reported in a recent paper.[1a] It was shown that an increase in the size of the chelate rings from five members to six members results in a substantial decrease in the magnitude of the stability constants of the metal chelates. Iminopropionic-acetic acid and aspartic acid, an isomer of iminodiacetic acid, are of interest because they represent structural forms intermediate to those of iminodiacetic and iminodipropionic acids. The production of a 1:1 complex would require the formation of five- and six-membered chelate rings within the same structure as opposed to two five-membered rings with iminodiacetic acid and two six-membered rings with iminodipropionic acid.

Although the behavior of aspartic acid with the alkaline earth metals has been investigated,[2-4]

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[1] F. C. Bersworth Postdoctoral Fellow, Clark University.

[1a] S. Chaberek, Jr., and A. E. Martell, THIS JOURNAL, **74**, 5052 (1952).

[2] S. Miyamoto and C. L. A. Schmidt, *J. Biol. Chem.*, **99**, 335 (1933).

[3] A. C. Batchelder and C. L. A. Schmidt, *J. Phys. Chem.*, **44**, 893 (1940).

[4] R. Lumb, Ph.D. Dissertation, Clark University, 1951.

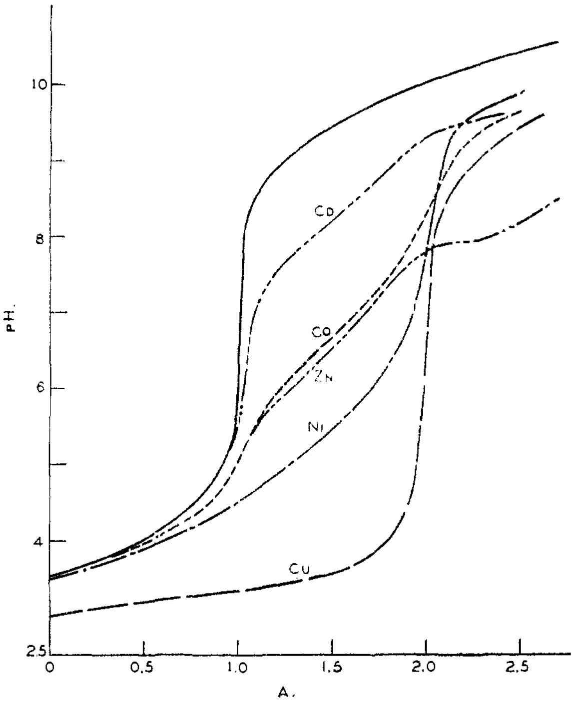


Fig. 1.—Titration curves of iminopropionic-acetic acid (IMPA) $C_A/C_M = 1/1$: $C_A$ and $C_M$ are total molar concentrations of amino acid and metal species, respectively; $A$ = moles of base added per mole of acid.

little work has been done with the corresponding transition metal complexes. Lumb[4] reported a stability constant of the 1:1 Cd complex to be 4.39. Li and Doody[5] determined polarographically the dissociation constant of cupric (aspartate)$_2$ ($6.3 \times 10^{-16}$). No work has been reported on iminopropionic-acetic acid.

## Experimental

The experimental method and conditions in the study of the dissociation and metal ion affinity of iminopropionic-acetic (IMPA) and aspartic (ASPA) acids is the same as that described in a previous publication.[1] The *dl*-aspartic acid used in this investigation was a C.P. sample purchased from the Pfanstiehl Chemical Company, and was used without further purification. Iminopropionic-acetic acid was synthesized by a method which will be described in a subsequent publication.[6]

The calculations were carried out in the same manner as has been described in the first paper of this series.[1] The acid dissociation constants were calculated by both the algebraic and modified Bjerrum methods. The 1:1 metal chelate titration curves were used for the calculation of stability constants by the algebraic method, and the 2:1 curves were utilized as a basis for the graphical Bjerrum method.

## Discussion of Results

**1:1 Titration Curves.**—The corrected titration curves for the amino acid in the presence and in the absence of an equivalent amount of metal ion are given in Figs. 1 and 2. The free acid curves (solid lines) are similar in shape and indicate a two-step ionization of a strong carboxyl group and a weak substituted ammonium group in the following way

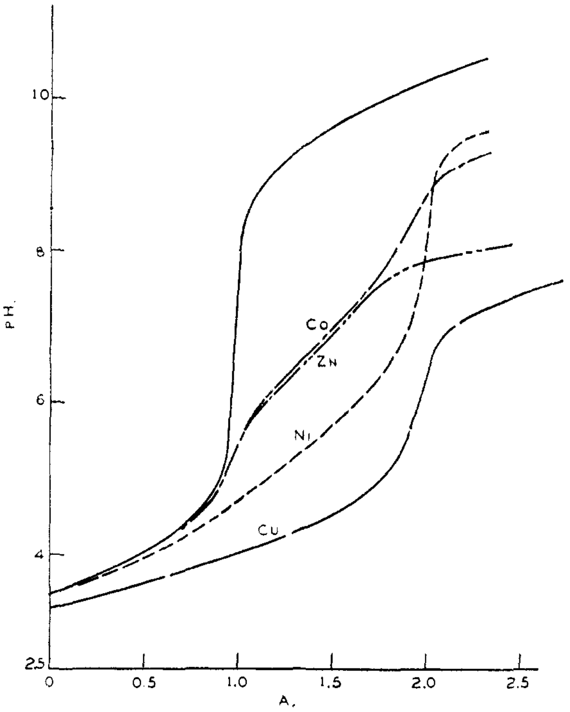
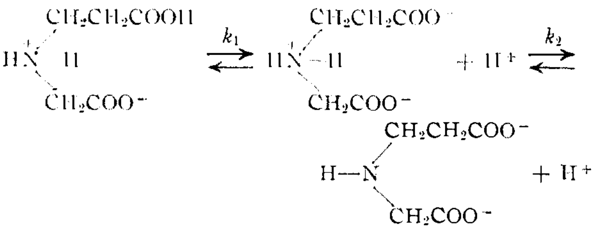
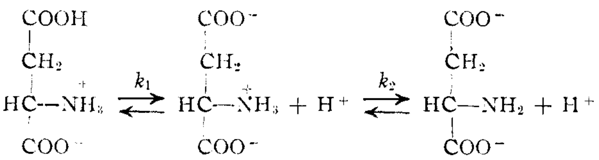


Fig. 2.—Titration curves of aspartic acid (ASPA) $C_A/C_M = 1/1$: $C_A$ and $C_M$ are total molar concentration of amino acid and metal species, respectively; $A$ = moles of base added per mole of acid.





$$\begin{array}{l}\text{COOH}\\ |\\ \text{CH}_2\\ |\\ \text{HC}-\overset{+}{\text{N}}\text{H}_3\\ |\\ \text{COO}^-\end{array} \overset{k_1}{\rightleftharpoons} \begin{array}{l}\text{COO}^-\\ |\\ \text{CH}_2\\ |\\ \text{HC}-\overset{+}{\text{N}}\text{H}_3\\ |\\ \text{COO}^-\end{array} + \text{H}^+ \overset{k_2}{\rightleftharpoons} \begin{array}{l}\text{COO}^-\\ |\\ \text{CH}_2\\ |\\ \text{HC}-\text{NH}_2\\ |\\ \text{COO}^-\end{array} + \text{H}^+$$

These curves are similar in shape to those of iminodiacetic and iminodipropionic acids, which also exhibit strong inflection points corresponding to the formation of the monopotassium salt.

The addition of an equivalent amount of metal ion lowers greatly the high $p$H buffer region. A little precipitation occurred in the vicinity of $a = 2$ for zinc and cadmium with iminopropionic-acetic acid. This was also true for the zinc aspartate titration curve. However, in all cases, the solution was homogeneous throughout the buffer regions. The general shape of the Zn, Co, Cd and Ni titration curves with both iminopropionic-acetic acid and aspartic acid are similar and correspond to the reaction

$$M^{+2} + HA^- \longrightarrow MA + H^+$$

where $H_2A$ represents iminopropionic-acetic and aspartic acids.

Interaction of these acids with cupric ions is greater than that with the other metals, and

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(5) N. C. Li and E. Doody, This Journal, **72**, 1891 (1950).

(6) S. Chaberek, Jr., F. C. Bersworth and A. E. Martell, unpublished results.

appreciable chelation occurs even in the strong acid region. Consequently, even the low $p$H buffer region is lowered according to the reaction

$$M^{+2} + H_2A \longrightarrow MA + 2H^+$$

However, this effect is appreciably greater for iminopropionic-acetic than for aspartic acid. The outstanding difference between the copper titration curves is the position of the higher $p$H buffer regions. The copper–iminopropionic-acetic acid curve had a strong inflection point at two equivalents of base characteristic of strong 1:1 complex formation. Little overlapping of $K_1$ and $K_2$ occurs, *i.e.*, the spreading factor between the consecutive constants is large. Apparently this effect is not as great for the copper aspartate curve. The buffer area exhibited by Cu–aspartate above $a = 2$ indicates appreciable interaction of MA and acid to form $MA_2$

$$MA + HA^- + OH^- \longrightarrow MA_2 + H_2O$$

**2:1 Titration Curves.**—The 2:1 titration curves (Figs. 3 and 4) further illustrate, first, the similarity of the Cd, Co, Zn and Ni curves and second, dissimilarity of the copper curves of iminopropionic acetic and aspartic acids. Small amounts of precipitates were formed at high $p$H with Zn and Cd–aspartate, and subsequent calculation of $\bar{n}$ values greater than $\bar{n} = 1.3$ was not possible. The general shapes and slopes of the Cd, Co, Zn and Ni complexes of the two amino acids are closely similar. Little or no complex formation occurs in the low $p$H region, and considerable overlapping occurs with these complexes.

The Cu–iminopropionic-acetic acid curve indicates that three protons are released per mole of metal ion before a strong inflection point occurs. This behavior is identical with that observed for the Cu-curves of iminodiacetic acid and iminodipropionic acid, and probably involves the formation of a strong 1:1 complex with the liberation of two protons, the third proton being liberated by the strongly acidic carboxyl group of the excess amino acid present. Further interaction occurring at

$$H_2A + M^{+2} + 2OH^- \longrightarrow MA + 2H_2O$$
$$H_2A + OH^- \longrightarrow HA^- + H_2O$$

$p$H above 7 results in the formation of the 2:1 complex, complete at $a = 4$. The dissimilarity of the 1:1 and 2:1 titration curves indicates that this step actually involves the formation of a 2:1 chelate rather than the addition of a hydroxide ion to the 1:1 chelate.

$$MA + HA^- + OH^- \longrightarrow MeA_2 + H_2O$$

The corresponding Cu–ASPA curve exhibits only a weak inflection point at four equivalents of base per mole of metal ion, and the intermediate region is a steep buffer region analogous to those exhibited by the other metals in the presence of aspartic acid.

**Formation Functions.**—The formation functions for iminopropionic-acetic and aspartic acids are plotted in Figs. 5 and 6. It was not possible to determine the second stability constant ($K_2$) for Cd and Zn aspartate directly from the $p$H value at $\bar{n} = 1.5$, since some precipitation occurred. However, it was calculated from the known value of $K_1K_2$ at $\bar{n} = 1.0$ and $K_1$ at $\bar{n} = 0.5$.

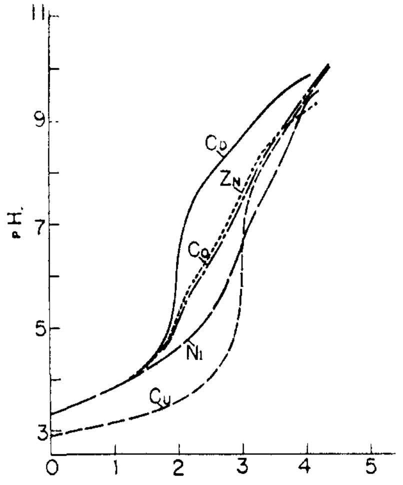

Fig. 3.—Titration curves of iminopropionic-acetic acid (IMPA) $C_A/C_M = 2/1$: $C_A$ and $C_M$ are total molar concentrations of amino acid and metal species, respectively; $M$ = moles of base added per mole of metal ion.

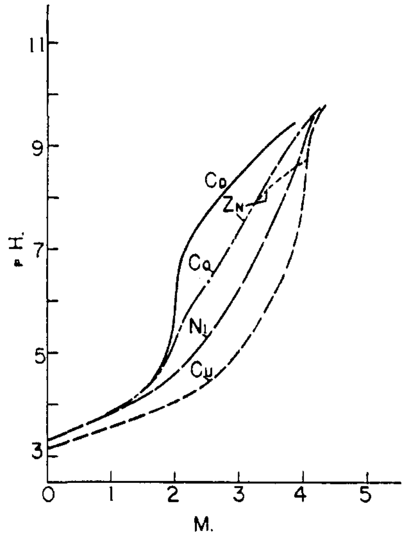

Fig. 4.—Titration curves of aspartic acid (ASPA) $C_A/C_M = 2/1$: $C_A$ and $C_M$ are total molar concentrations of amino acid and metal species, respectively; $M$ = moles of base added per mole of metal ion.

**Acid Dissociation Constants.**—The magnitudes of the acid dissociation constants of iminopropionic-acetic and aspartic acids listed in Table I are quite similar. The aspartic acid values are slightly lower than those reported by Lumb[4] ($pK_1$ 3.67, $pK_2$ 9.62), but agree well with those reported by Schmidt, Kirk and Applemen[7] ($pK_1$ 3.61, $pK_2$ 9.47).

It is also interesting to note that their acid strengths are intermediate to those of iminodiacetic acid ($pK_1$ 2.54, $pK_2$ 9.12) and iminodipropionic acid ($pK_1$ 4.11, $pK_2$ 9.61). This is not surprising in view of the fact that they also represent intermediate structural types.

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(7) C. L. A. Schmidt, P. L. Kirk and W. K. Applemen, *J. Biol. Chem.*, **88**, 285 (1930).

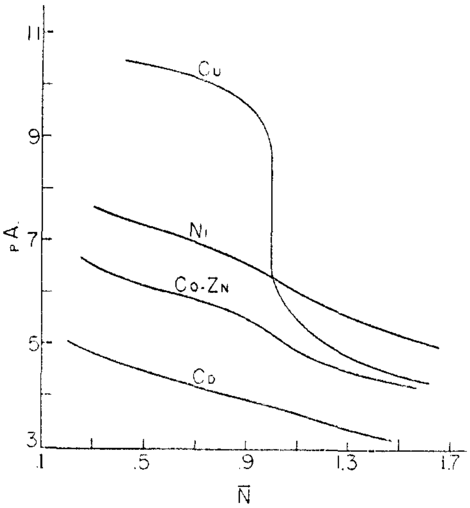


Fig. 5.—Formation functions of iminopropionic-acetic acid (IMPA): $\bar{N}$ = average number of ligands bound per mole of metal ion; $p$A = negative logarithm of anion, $A^{-2}$, concentration.

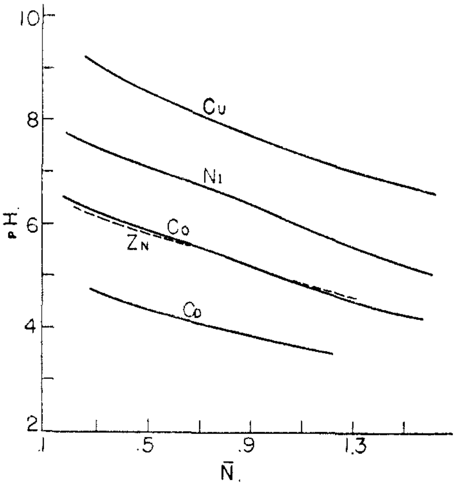


Fig. 6.—Formation functions of aspartic acid (ASPA): $\bar{N}$ = average number of ligands bound per mole of metal ion; $p$A = negative logarithm of anion, $A^{-2}$, concentration.

Table I

Equilibrium Constants

$T = 30°$, $\mu = 0.1$, $\gamma_{H^+} = 0.78$

| Iminopropionic-acetic acid $pK_1 = 3.61$; $pK_2 = 9.46$ | | | | Aspartic acid $pK_1 = 3.68$; $pK_2 = 9.46$ | | | |
|---|---|---|---|---|---|---|---|
| | Bjerrum method | | Algebraic method | | Bjerrum method | | Algebraic method |
| $M^{+2}$ | log $K_1$ | log $K_2$ | log $K_1$ | $M^{+2}$ | log $K_1$ | log $K_2$ | log $K_1$ |
| $Cu^{+2}$ | 10.45 | 4.45 | 10.52 | $Cu^{+2}$ | 8.57[c] | 6.78 | 8.50 |
| $Ni^{+2}$ | 7.35 | 5.23 | 7.33 | $Ni^{+2}$ | 7.12 | 5.27 | 7.07 |
| $Co^{+2}$ | 6.17 | 4.29 | 6.13 | $Co^{+2}$ | 5.90 | 4.28 | 5.85 |
| $Zn^{+2}$ | 6.17 | 4.31 | 6.25 | $Zn^{+2}$ | 5.84 | 4.31[a] | 5.78 |
| $Cd^{+2}$ | 4.52 | 3.16 | 4.55 | $Cd^{+2}$ | 4.37[b] | 3.11[a] | .. |

[a] Calculated from (log $K_1$ + log $K_2$) from $\bar{n}$ = 1.0 and known $K_1$ at $\bar{n}$ = 0.5. [b] Lumb[4] reports log $K_1$ = 4.39. [c] From data of Li and Doody[5] (log $K^1$ + log $K_2$ = 15.3); these results (log $K_1$ + log $K_2$) = 15.3.

**Stability Constants.**—The successive chelate stability constants calculated by the Bjerrum method for iminopropionic-acetic acid and aspartic acid with various metals, and the 1:1 chelate stability constants calculated by the algebraic method previously described are listed in Table I. Comparison between the chelating tendencies of these chelating agents with the structurally related compounds, iminodiacetic and iminodipropionic acids are made in Table II.

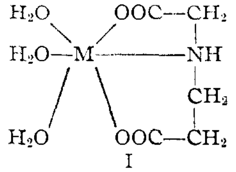
Table II

Relative Values of Successive Formation Constants of Dicarboxylicmonoamino Acid Chelates

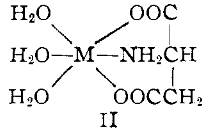
$\Delta$ = log $K_1$ − log $K_2$

| $M^{+2}$ | IMDA | IMPA | ASPA | IMDP |
|---|---|---|---|---|
| $Cu^{+2}$ | 4.90 | 6.00 | 1.79 | 5.68 |
| $Ni^{+2}$ | 1.86 | 2.12 | 1.85 | 2.37 |
| $Co^{+2}$ | 1.61 | 1.88 | 1.62 | 1.66 |
| $Zn^{+2}$ | 1.89 | 1.86 | 1.53 | .. |
| $Cd^{+2}$ | 1.17 | 1.36 | 1.26 | .. |

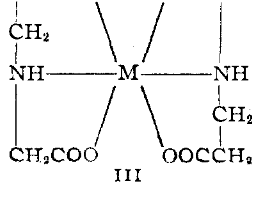
The general order of stability of the 1:1 chelates of iminopropionic-acetic and aspartic acids is Cu > Ni > Co, Zn > Cd, the same as that reported for iminodiacetic and iminodipropionic acids. The relative magnitudes of the second chelate formation constants, $K_2$, is Ni > Cu, Co, Zn > Cd for all these acids excepting aspartic acid, for which the order of stabilities is: Cu > Ni > Co, Zn > Cd. For each metal ion, with the exception of Cu, the stabilities of the iminopropionic-acetic and aspartic acid chelates are approximately equivalent, and are intermediate between the values of the corresponding chelates of iminodiacetic and iminodipropionic acids. The fact that the values of $K_1$ and $K_2$ for a particular metal (except copper) are approximately equal for iminopropionic-acetic and aspartic acids is interesting in view of the fact that the basicities of these two amino acids, as measured by their acid dissociation constants, are the same. This indicates that the differences in the steric arrangements of the donor groups in these two analogous chelating agents has no effect on their chelating tendencies toward all the metals investigated excepting copper. The stabilities of these chelates are intermediate between those of iminodiacetic and iminodipropionic acid, which have been previously shown to be tridentate chelating agents.[1] In view of the fact that the basicities of the chelating anions of the present investigation are also intermediate between those of iminodiacetate and iminopropionate ions, there can be little doubt that the chelates of iminopropionic-acetic and aspartic acid with metals of coördination number 6 are also tridentate, as indicated by formulas I, II, III and IV.



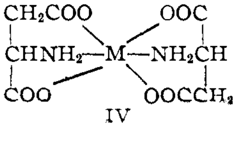
I



II



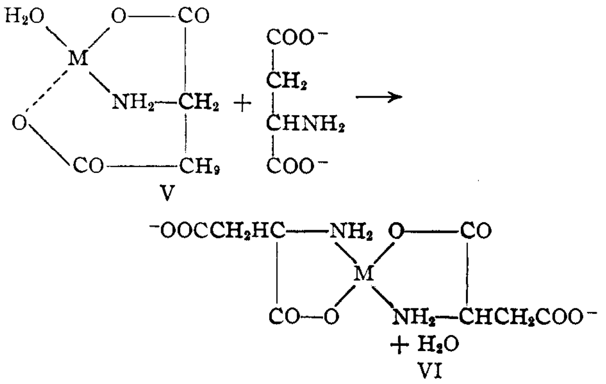
III



IV

It is apparent from the results in Table II that except for the aspartic acid chelates the ratio of the first to the second chelate stability constant is much greater for copper than for the other metals investigated. This is due to the fact that the coördination number of copper is four, and one mole of a tridentate chelating agent satisfies all but one of the coördination requirements of the metal. Hence it is to be expected that the difference between the first and second stability constants will be much greater than normal.

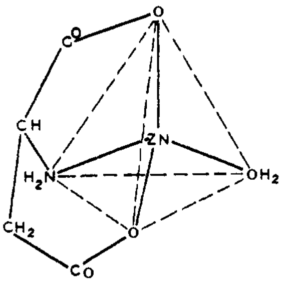
In the case of aspartic acid, it is apparent from formula V that, if it behaves as a tridentate reagent, it cannot satisfy three of the square planar copper covalencies without introducing considerable strain in the chelate rings. Thus the stability of V would be less than that expected for a tridentate structure. Combination of V with a second donor anion may be considered as taking place in the manner indicated by the equation



V

VI

The binary chelate VI which results contains two very stable α-amino acid rings and the equilibrium constant for the reaction would be expected to be quite large. Thus the abnormally low stability of V favors a comparatively low value for $K_1$ and a relatively high value for $K_2$, compared to the behavior of other metals. Although $Zn^{+2}$ also has a coördination number of 4, the equilibrium constants listed in Table II indicate its behavior to be more nearly normal with respect to the stability of the aspartic acid chelates. This is probably due to the fact that the structure is tetrahedral, and that the chelate rings formed involve very little, if any, strain, as is indicated by formula VII.



VII

With the exceptions noted above, both the first and second metal chelate stability constants of iminopropionic-acetic and aspartic acids lie approximately half way between the corresponding metal chelate stability constants of the analogous compounds, iminodiacetic acid and iminodipropionic acid.

**Acknowledgment.**—The authors are indebted to the Bersworth Chelate Research Organization for a grant which made this work possible.

WORCESTER, MASSACHUSETTS

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[CONTRIBUTION NO. 31 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

# Thiacyclopentane: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy, Heat of Formation and Thermodynamic Functions[1]

BY W. N. HUBBARD, H. L. FINKE, D. W. SCOTT, J. P. MCCULLOUGH, C. KATZ, M. E. GROSS,
J. F. MESSERLY, R. E. PENNINGTON AND GUY WADDINGTON

RECEIVED JUNE 20, 1952

The following thermodynamic properties of thiacyclopentane were determined experimentally: heat capacity of the solid and liquid between 13 and 333°K., triple point (176.98°K.), heat of fusion (1757 cal. mole$^{-1}$), vapor pressure [$\log_{10} p = 6.99540 - 1401.939/(t + 219.607)$ ($p$ in mm. and $t$ in °C.)], heat of vaporization (8820, 8589 and 8279 cal. mole$^{-1}$ at 349.86, 370.16 and 394.28°K., respectively), heat capacity of the vapor [$C_p^\circ = -8.23 + 0.1192T - 6.551 \times 10^{-5} T^2$ cal. deg.$^{-1}$ mole$^{-1}$ (378–487°K.)], second virial coefficient [$B = V - RT/P = -295 - 32.37 \exp(1250/T)$ cc. mole$^{-1}$], entropy of the liquid (49.67 cal. deg.$^{-1}$ mole$^{-1}$ at 298.16°K.), entropy of the vapor ($S^\circ$ = 77.72, 79.22 and 80.92 cal. deg.$^{-1}$ mole$^{-1}$ at 349.86, 370.16 and 394.28°K., respectively) and heat of formation [for the reaction: 4C (graphite) + $4H_2$ (g) + S(rhombic) = $C_4H_8S$(liq), $\Delta H^\circ_{298.16} = -17.4$ kcal. mole$^{-1}$]. The functions $-(F^\circ - H^\circ_0)/T$, $(H^\circ - H^\circ_0)/T$, $H^\circ - H^\circ_0$, $S^\circ$ and $C^\circ_p$ were computed by the methods of statistical mechanics for selected temperatures up to 1000°K. Values of the heat, free energy and equilibrium constant of formation of thiacyclopentane were obtained for the same temperatures.

This Laboratory is engaged in an investigation of the thermodynamic properties of organic sulfur compounds because of their importance in petroleum technology. The program entails making detailed studies of individual compounds that are representative of the types of sulfur compounds that occur in crude petroleum or are produced in refining processes. The investigations on a given compound include a variety of experimental measurements, mostly calorimetric, the results of which, whenever possible, are correlated and extended by the methods of statistical mechanics to give relatively completely thermodynamic information for the whole temperature range of practical interest.

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(1) This investigation was part of the work of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurement of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.