The Stability of Fused Rings in Metal Chelates. II. Copper(II) Complexes of Schiff Bases Derived from Pyruvic Acid and Amino Acids or Diamines[1]

By Akitsugu NAKAHARA, Haruyo YAMAMOTO and
Hironobu MATSUMOTO

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It has long been observed that an increase in the number of rings within a particular chelate structure results in the greater stability of the chelate. For example, when Calvin and Bailes[2] studied polarographically the relationship between structure and stability for the salicylaldimine copper(II) chelates, they conculded that the effect of tying together the coordinating groups to form additional rings is most essential in stabilizing the chelate. The same trend was also pointed out by Schwarzenbach[3] for a number of zinc complexes from a comparison of their formation constants. No attempt has, however, yet been made to investigate systematically how the structural factors of individual rings in a metal polydentate influence the stability of the whole fused-ring system.

The present paper is a report on a more or less quantitative survey to determine the influence of an alteration of the size of individual rings upon the stability of the fused-ring system in copper(II)-Schiff base chelates. Spectroscopic and polarographic methods were applied to determine the relative stability of those chelates. Glycine, β-alanine, ethylenediamine and trimethylenediamine were selected as amino compounds to form Schiff bases with carbonyl compounds, such as pyruvic acid, acetylacetone and salicylaldehyde. Consequently, we have succeeded in isolating four new copper(II) complexes derived from pyruvic acid. The preparation and properties of these new chelates will also be described in this paper.

Experimental

The Preparation of Copper(II) Chelates.—*Copper(II) Chelate of the Schiff Base Derived from Pyruvic Acid and Glycine, A.*—To a solution of 12.5 g. of glycine in 50 ml. of aqueous ethanol (two to one by volume mixture) was added 14.3 g. of pyruvic acid. The resulting mixture was stirred and heated at about 40°C. To this was added 33.3 g. of copper(II) acetate monohydrate. The reaction mixture was kept at 40°C for about two more hours while being constantly stirred. A dark blue solution was gradually obtained, accompanied by a precipitation of pale blue microscopic crystals. The precipitate was filtered by suction and recrystallized from a small amount of water.

The final pure product appears as thin, pale blue plates which begin to decompose at 192°C. The compound is soluble in water and is slightly soluble in ethanol, but it is insoluble in acetone

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[1] Part I of this series: A. Nakahara, H. Yamamoto and H. Matsumoto, *Sci. Rep., College of Gen. Ed., Osaka Univ.*, **12**, 11 (1963).

[2] M. Calvin and R. H. Bailes, *J. Am. Chem. Soc.*, **68**, 949 (1946).

[3] G. Schwarzenbach, *Chimia* (*Buenos Aires*), **3**, 1 (1949).

or chloroform.

Found: C, 23.13; H, 4.23; N, 5.57; H_2O, 20.50. Calcd. for dihydrate of A, $[Cu(pyv{=}gly)(H_2O)]\cdot 2H_2O$: C, 23.00; H, 4.21; N, 5.36; H_2O, 20.65%.

Copper(II) Chelate of a Schiff Base Derived from Pyruvic Acid and β-Alanine, B.—To a solution of 6.5 g. of β-alanine in 50 ml. of water 6.4 g. of pyruvic acid was added. The mixture was stirred and heated at about 45°C. To this was added copper(II) hydroxide or oxide freshly precipitated from an aqueous solution containing 20 g. of copper(II) sulfate pentahydrate. The resulting mixture was kept at 45°C for about five hours while being constantly stirred. The color of the solution gradually changed from dark green to bluish geen. The solution was then filtered to remove unreacted copper(II) hydroxide and was allowed to stand at 0°C. Beautiful blue monoclinic crystals were obtained after 24 hr. The compound was found to decompose at 210°C. The compound is soluble in water and ethanol, but it is insoluble in acetone or chloroform.

Found: C, 26.15; H, 4.64; N, 5.11; H_2O, 19.43. Calcd. for dihydrate of B, $[Cu(pyv{=}\beta\text{-}ala)(H_2O)]\cdot 2H_2O$: C, 26.20; H, 4.73; N, 5.09; H_2O, 19.65%.

Copper(II) Chelate of the Schiff Base Derived from Pyruvic Acid and Ethylenediamine, C.—To a solution of 7.5 g. of ethylenediamine in 100 ml. of methanol in an ice-bath, 22 g. of pyruvic acid was gradually added. After the completion of a vigorous reaction, the resulting mixture was stirred and heated at about 50°C. Hereupon an yellowish orange precipitate resulting from the formation of the Schiff base was obtained. The precipitate was filtered by suction and dissolved in 100 ml. of water without further purification. To this was added cupric oxide freshly precipitated from an aqueous solution containing 35 g. of copper(II) sulfate pentahydrate. The resulting mixture was kept at 50°C for two hours while being constantly stirred. The reaction mixture was filtered while it was warm. A large amount of acetone was then added to the filtrate. Hereupon, a dark green, crystalline solid was deposited. To purify the chelate, the above procedure of adding a large amount of acetone to the concentrated aqueous solution of the chelate was repeated several times. Since the compound which had not completely dried readily became sticky on being exposed to air, in order to accomplish complete dehydration it was necessary to dry the compound in vacuo for three days.

The compound appears green and was found to decompose at 184°C. The compound is soluble in water but insoluble in common organic solvents.

Found: C, 37.92; H, 4.26; N, 10.42. Calcd. for C, $[Cu(pyv{=}en{=}pyv)]$: C, 36.71; H, 3.82; N, 10.71%.

Copper(II) Chelate of the Schiff Base Derived from Pyruvic Acid and Trimethylenediamine, D.—To a solution of 8.8 g. of trimethylenediamine in 10 ml. of water 22 g. of pyruvic acid was added. The solution changed to yellowish orange on account of the formation of the Schiff base. To this was added copper(II) hydroxide or oxide freshly precipitated from an aqueous solution containing 32 g. of copper(II) sulfate pentahydrate. The resulting mixture was kept at 45°C for three hours while being constantly stirred and was then filtered. When the solution was allowed to stand at 0°C, blue crystals were deposited. These were recrystallized from water to give beautiful needles which decompose at 208°C. The compound is soluble in water and pyridine, but insoluble in ethanol, acetone and chloroform.

Found: C, 36.54; H, 4.75; N, 9.61. Calcd. for monohydrate of D, $[Cu(pyv{=}trim{=}pyv)]\cdot H_2O$: C, 36.85; H, 4.77; N, 9.54%.

Copper(II) Chelates of Schiff Bases Derived from Acetylacetone and Diamines, E and F. — These two chelates were prepared according to the directions of McCarthy et al.[4] The compound E in the crystalline state appears purple right after the recrystallization from methanol, but when it comes in contact with water vapor, when allowed to stand in the atmosphere, it gradually changes green. This is probably because of an additional coordination of the water molecule around copper(II), as has been demonstrated for the copper(II) chelates of salicylaldehyde-Schiff bases.[5,6]

On the other hand, the compound F only appears green in spite of having no crystal water. The compound E was found decompose at 144°C, while F decomposed at 97°C. Both the two compounds are readily soluble in common organic solvents but only slightly soluble in water.

Copper(II) Chelates of Schiff Bases Derived from Salicylaldehyde and Diamines, G and H. — These two chelates were prepared by the method of Pfeiffer et al.[7] from a mixture of 1:2:1 copper(II): salicylaldehyde: ethylene- or trimethylenediamine. No decomposition was observed, at least below 260°C, for these two compounds. The chelate G is green in the crystalline state, purple in a chloroform solution and bluish green in a pyridine solution. It is insoluble in water, ethanol and acetone. On the other hand, the chelate H is purple in the crystalline state and green in chloroform and pyridine solutions. The color of these chelates is apparently closely related to the additional coordination of solvent molecules around copper(II) as well as to their original chelate structure. This point, however, awaits further investigation.

Spectroscopic Measurements. — The visible and ultraviolet absorption spectra of the chelates were determined with a Shimadzu spectrophotometer Type QB-50 at room temperature. The solvent used here was water in all cases, and the concentrations of the solutions varied from 10^{-3} to 10^{-5} M.

Polarographic Measurements. — Measurements were made with a Yanagimoto recording polarograph model PA-102. An "H" cell was used, the reference electrode being a saturated calomel electrode and the whole cell being thermostated at 25±0.5°C.

Pure distilled mercury was used throughout. C. p. chemicals were used in all cases. Tank nitrogen was bubbled without any further purification

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[4] P. J. McCarthy, R. J. Hovey, K. Ueno and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 5820 (1955).

[5] F. J. Llewellyn and T. N. Waters, *J. Chem. Soc.*, **1960**, 2639.

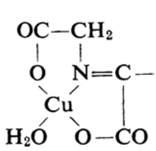
[6] T. Tanaka, This Bulletin, **29**, 93 (1956).

[7] P. Pfeiffer, E. Breith, E. Lübbe and T. Tsumaki, *Ann.*, **503**, 85 (1933).

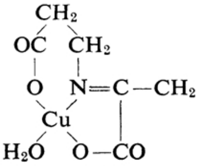
through the samples to remove dissolved oxygen. The concentration of the copper(II) chelates varied from 10^{-4} to 10^{-3} M. The supporting electrolyte used was 0.1 M potassium nitrate in all cases. As for the maximum suppressor, methyl red was employed in all cases. A point was plotted for each individual drop on the rising part of the curve, and at least six values were used along the mid-portion of the curve. The plot of log $i/(i_d-i)$ against the voltage invariably resulted in a straight line with an allowable scatter of points and a slope of either nearly 0.06 or 0.03. The half-wave potential was taken as that value of the voltage for which the log term was zero.

Results and Discussion

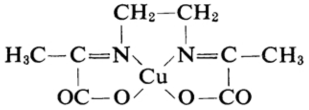
As was described in the preceding section, pyruvic acid condenses in the presence of copper(II) with glycine, β-alanine, ethylenediamine and trimethylenediamine, giving rise to the respective copper(II)-Schiff base chelate. It seems quite reasonable to assign the following structures, A → D, to the four copper(II) chelates on the basis of the analytical data and the quadri-coordinating character of copper(II) complexes.



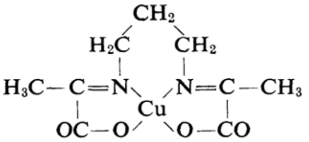
(A)
[Cu(pyv=gly)(OH$_2$)]



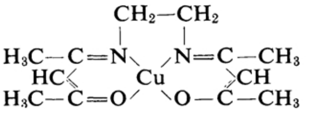
(B)
[Cu(pyv=β-ala)(OH$_2$)]



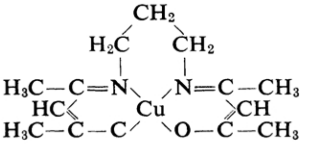
(C)
[Cu(pyv$_2$=en)]



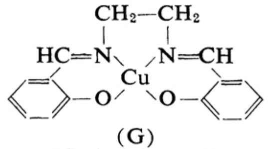
(D)
[Cu(pyv$_2$=trim)]



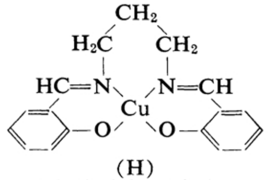
(E)
[Cu(acac$_2$=en)]



(F)
[Cu(acac$_2$=trim)]



(G)
[Cu(salal$_2$=en)]



(H)
[Cu(salal$_2$=trim)]

The difference in structure between A and B, or between C and D, is only the number of methylene groups in the same part of the organic residues. The four atoms bound to copper(II) are exactly the same in each pair. In other words, the skeletal structure of A consists of two adjacent five-membered rings, 5–5,* while that of B is five- and six-membered rings, 5–6.* In the same way, the skeletal structures of C and D are expressed as 5–5–5 and 5–6–5 respectively.

From a comparison of the properties of the respective aqueous solution, A is considered to be less stable than B. For instance, A is more difficult to recrystallize from water than B because it is accompanied by a decomposition to some extent in an aqueous solution. A slight difference is observed also in a comparison of their decomposing temperatures, as is shown in Table I.

Since the decomposing temperature of A is distinctly lower than that of B, the same relationship in relative stability, A<B, is supported here again. This situation seems to be characteristic of this type of fused-ring system, since it has been known that glycine generally forms a more stable chelate ring than β-alanine.[8-10] The same characteristic is observed also in a comparison of the other pair, C and D. Trimethylenediamine seems to be more favorable than ethylenediamine to forming stable interlocked rings around copper(II) between two pyruvate residues, unlike when they are respectively coordinated to a metal to form a single ring.[11,12] The difference in stability is observed to be much greater in

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* Hereafter the notation "5-5" will be adopted for this type of fused rings. In the same manner, the fused rings in B, C and D will be expressed as 6-5, 5-5-5 and 5-6-5 respectively.

8) A. Nakahara, This Bulletin, **29**, 925 (1956).

9) C. B. Monk, *Trans. Faraday Soc.*, **47**, 285 (1951).

10) R. M. Keefer, *J. Am. Chem. Soc.*, **68**, 2329 (1946).

11) P. Pfeiffer and E. Lübbe, *J. Prakt. Chem.*, [2], **136**, 321 (1933).

12) M. Calvin and A. E. Martell, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York (1952), p. 522.

this particular case, C<D. While D is readily recrystallized from hot water to give typical beautiful crystals, C is not satisfactorily recrystallized from any solvent, as has been described in the preceding section. The same order in stability is confirmed from a comparison of their decomposing temperature, as is shown in Table I.

The influence of the ethylene- and trimethylene-diamine chelate rings upon the stability of the respective fused-ring system, however, is reversed in the case of the acetylacetone- or salicylaldehyde-Schiff base complex, as is clear from Table I, E>F, G>H. The evidence for this is not obtainable from the same preliminary tests as employed above, but it is given by spectroscopic and polarographic data, as will be discussed in the later part of this paper. At any rate, ethylenediamine is considered to have an advantage over trimethylenediamine in forming fused rings around copper(II) with two acetylacetone or salicylaldehyde residues. This is probably a very important example to demonstrate the influence of the alteration of the size of individual rings upon the stability of the whole fused-ring system in metal polydentates. That is to say, a five-membered ring stabilizes the fused-ring system more than a six-membered ring does when either is respectively located between two six-membered rings, while the same five-membered ring stabilizes the fused-ring system less than the six-membered ring does when either is located between two five-membered rings, (5–5–5<5–6–5, 6–5–6>6–6–6).

Hence, it may be concluded that the stability of a fused-ring can not be predicted from the simple summation of the stabilty of the individual rings contained in the fused-ring system. It is considered that this is because no stress on any individual ring in metal polydentate chelates is deposited in the same ring; rather, it spreads to some extent over the whole fused-ring system, being sometimes strengthened and at other times weakened or even completely cancelled by another stress on another ring in the system.

After all, the stability of metal polydentate chelates increases with the decreasing stress over the whole fused-ring system.

For example, ethylenediamine, which is located between two pyruvate rings as a bridge in a polydentate ligand, does not weaken the stress on the adjacent copper-pyruvate rings, probably because of its too short chain, but trimethylenediamine is supposed to be long enough to weaken the stress in such a case. The above consideration can easily be supported by a simple test making use of the Stuart model. On the other hand, if the adjacent metal chelate rings are six-membered rings, such as metal-acetylacetone or -salicylaldehyde, it is not necessary to assume a significant stress on those metal-chelate rings. Hence, trimethylenediamine, which is located between two those six-membered rings, would preferably be unfavorable to forming a stable structure because of its too long chain. Ethylenediamine may fit in such a situation contrary to the above case. The greater stability of the β-alanine-pyruvate complex, B, compared with the glycine-pyruvate complex, A, is explainable from the same point of view.

Spectroscopic Studies.—It is also of interest to compare the relationship between the structure and the light absorption for those copper(II) chelates. The color of A is pale bule, while that of B is a little more intense blue. The chelate C appears green, while D appears blue. This is a great difference compared with their difference in structure.

The visible and ultraviolet absorption spectra

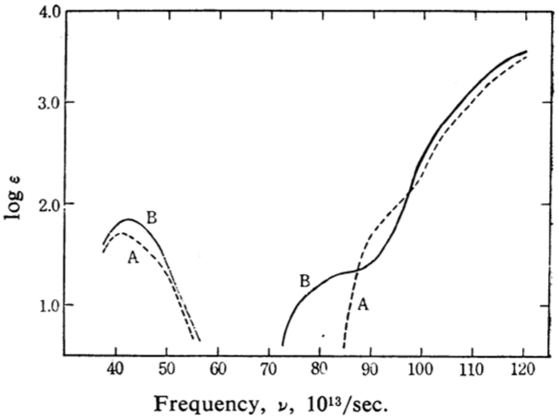

Fig. 1. Absorption spectra of copper(II)-chelates, A [$Cu(pyv=gly)(OH_2)$], and B [$Cu(pyv=\beta\text{-}ala)(OH_2)$].

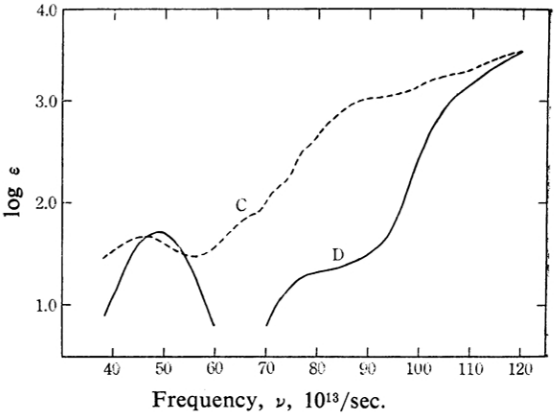

Fig. 2. Absorption spectra of copper(II)-chelates, C [$Cu(pyv=en=pyv)$], and D [$Cu(pyv=trim=pyv)$].

TABLE I. PROPERTIES OF COPPER(II)-SCHIFF BASE COMPLEXES

	Schiff base (ligand)	Skeletal structure of fused rings	Color and melting (or decomposing) point	Absorption maximum (ν_{max} in 10^{13}/sec. and log ε_{max}) in the visible region	Half-wave potential $E_{1/2}$ vs. SCE at 25°C
(A)	Pyruvic acid and glycine	5–5	Pale blue (cryst.) Pale blue (aq. soln.) 192∼206°C (decomp.)	ν, 41.4 log ε, 1.70	$E_{1/2}^{(1)}$, -0.11 V. $E_{1/2}^{(2)}$, -0.37 V. two-step reduction
(B)	Pyruvic acid and β-alanine	6–5	Blue (cryst.) Blue (aq. soln.) 210∼213°C (decomp.)	ν, 42.3 log ε, 1.85	$E_{1/2}^{(1)}$, -0.22 V. $E_{1/2}^{(2)}$, -0.35 V. two-step reduction
(C)	2 : 1 Pyruvic acid : Ethylenediamine	5–5–5	Green (cryst.) Green (aq. soln.) 184°C (decomp.)	ν, 46.1 log ε, 1.68	$E_{1/2}$, -0.29 V., irrev.
(D)	2 : 1 Pyruvic acid : Trimethylenediamine	5–6–5	Blue (cryst.) Blue (aq. soln.) 208°C (decomp.)	ν, 48.8 log ε, 1.72	$E_{1/2}$, -0.51 V., one-step reduction
(E)	2 : 1 Acetylacetone : Ethylenediamine	6–5–6	Green (hydrate cryst.) Violet (non-hydrate cryst.) Violet (solution) 144°C (m. p.)	ν, 55.6 log ε, 2.13	$E_{1/2}$, -1.12 V., irrev.
(F)	2 : 1 Acetylacetone : Trimethylenediamine	6–6–6	Green (cryst.) Green (aq. soln.) 97°C (m. p.)	ν, 50.8 log ε, 2.05	$E_{1/2}$, -0.79 V., irrev.
(G)	2 : 1 Salicylaldehyde : Ethylenediamine	6–5–6	Green (cryst.) Violet (in chloroform) Bluishgreen (in pyridine)	ν, 53.1 log ε, 2.55 (in $CHCl_3$)	$E_{1/2}$, -0.94 V., irrev. (0.1 M KNO_3 50% H_2O-pyridine)
(H)	2 : 1 Salicylaldehyde : Trimethylenediamine	6–6–6	Violet (cryst.) Green (in chloroform) Green (in pyridine)	ν, 49.6 log ε, 2.37 (in $CHCl_3$)	$E_{1/2}$, -0.66 V., irrev.

of those four chelates in an aqueous solution are shown in Fig. 1 (A and B), and in Fig. 2 (C and D), while their numerical data are shown in Table I.

It is expected that the greater the stress through the fused-ring system, the greater the weakening of the ligand field around copper(II). Moreover, the weakening of the ligand field is supposed to be reflected in the degree of bathochromic shifting of the absorption band.

Therefore, the ligand-field absorption band in each spectrum may be considered to be a measure of the stability of those chelates. From this point of view, a more or less quantitative survey may be made on the basis of spectroscopic studies to decide the influence of the alteration of the size of individual rings upon the stability of the whole fused-ring system in copper(II) chelates. The stability order, (A) 5–5<(B) 5–6; (C) 5–5–5<(D) 5–6–5, is confirmed here again by the results of the spectroscopic investigation. As to the acetylacetene-Schiff base chelates, the same stability order as mentioned above, (E) 6–5–6>(F) 6–6–6, is reaffirmed in the same way.

Polarographic Studies. — A comparison of half-wave potentials for the same type of complexes under the same conditions may be an important approach to ascertaining the relative stability of the complexes against the reduction at the dropping mercury electrode. Of course, the more negative the value of the half-wave potential, the greater the stability of the complex. The numerical data are summarized in Table I.

It is necessary to consider at least two electrode reactions for the cases of the comparatively unstable chelates, such as A, B, C and D: (1) the direct reduction of the copper(II) chelate; and (2) the reduction of unchelated Cu^{2+}, which is produced by the dissociation of the copper(II) chelate. This is because each polarogram more or less contains a reduction wave which coincides with that of the simple cupric ion as well as with that of the copper(II) chelate concerned. Since, however, the redution wave of simple cupric ion* mostly appears considerably away from that of the chelated copper(II), there was no interference with the determination of the half-wave potentials.

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* The half-wave potential of the simple cupric ion for the reduction of Cu^{2+} to Cu^0 was determined to be +0.05 V. vs. SCE at 30°C in a 0.1 M potassium nitrate solution containing 0.01% gelatine.

On the other hand, it is unnecessary to take the decomposition of complexes into account for the cases of fairly stable chelates such as E and F, since the dissociation is slow compared to the direct reduction of the chelate at the electrode. The absorption spectra of those very stable chelate solutions also showed no indications of dissociation occurring.

The half-wave potential presented by Calvin and Bailes.[2] for the copper(II) chelate of salicylaldehyde-ethylenediamine, G, is -0.75 V., showing a considerable discrepancy with the present value, -0.94 V. (cf. Table I). This is understandable when we remember the difference in the conditions applied in the respective measurements. In the present work, the measurements for G and H were made with a 0.1 M potassium nitrate solution of a 50% (by volume) mixture of pyridine and water, using methyl red as the maximum suppressor. Calvin and Bailes used hydrochloric acid instead of potassium nitrate, and used no maximum suppressor. At any rate, it is not significant to discuss the cases of G and H quantitatively since they are certainly not reversible waves. At the same time, it is not necessary to know the precise values of the half-wave potentials in all cases either, since our present purpose is a qualitative comparison of the effects of changes in structure upon the nature of the chelate. However, all the polarograms other than those of G and H are supposed to be at least good enough for a semi-quantitative discussion.

The order in stability established by the polarographic studies shows a precise coincidence with that obtained from preliminary tests or spectroscopic studies previously described: (A) 5–5$<$(B) 6–5; (C) 5–5–5$<$(D) 5–6–5; (E) 6–5–6$>$(F) 6–6–6; (G) 6–5–6$>$(H) 6–6–6.

Summary

The preparation and some properties of four new copper(II) chelates of Schiff bases produced from pyruvic acid and amino acids or diamines have been reported.

The relative stability of these compounds as well as of other rather popular copper(II) chelates has been discussed on the basis of spectroscopic and polarographic investigations.

It has been demonstrated that any stress on any individual ring in metal polydentate chelates does not generally tend to be deposited in the same ring, but rather spreads to some extent over the whole fused-ring system, sometimes strengthened and at other times weakened or even completely cancelled by another stress on another ring in the system. Therefore, the stability of fused rings should not be discussed on the basis of a simple summation of the stability of individual rings contained in the fused-ring system. It has been concluded that the stability of metal polydentate chelates increases with a decrease in stress over the whole fused-ring system.

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Institute of Chemistry
College of General Education
Osaka University
Toyonaka, Osaka