Copper(II) Chelates of Schiff Bases Derived from Salicylaldehyde and Various α-Amino Acids

Yasuo NAKAO, Ken-ichi SAKURAI and Akitsugu NAKAHARA

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

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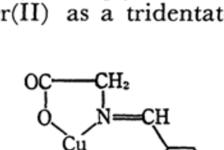
The metal complexes of Schiff bases derived from salicylaldehyde and amino acids[1-3] have received comparatively little attention, in spite of their apparent usefulness as models for the more complicated metal-pyridoxal-amino acid systems, which are the intermediates in biologically important transamination reactions.[4,5] From this point of view, the preparation and characterization of *N*-salicylideneglycinatoaquocopper(II) were reported in an earlier paper.[6] Very recently, Burrows and Bailar[7] have published the paper on the preparation of iron(III) and cobalt(III) complexes of some *N*-salicylideneamino acids. The present paper describes the preparation and chemical structure of a series of new copper(II) chelates of similar Schiff bases listed in Table 1.

As reported previously[6], the preparation of *N*-salicylideneglycinatoaquocopper(II) is achieved successfully by the reaction of glycine with bis(salicylaldehydato)copper(II) as well as by the direct reaction of glycine, salicylaldehyde and copper(II). In this work, the former method was applied in all cases. All the complexes are easily recrystallized from water or aqueous ethanol as beautiful needles or plates, and appear light green to dark green. In the crystalline state they are quite stable at room temperature and, with the exception of α-aminoisobutyrate- and aspartate-Schiff base, are decomposed at about 200—230°C. The results of elemental analyses and some numerical data for the spectrophotometric measurements are listed in Tables 1 and 2, respectively. Inspection of Table 2 reveals that there are no remarkable differences between the wavelengths for the maxima of the respective absorption bands due to the ligand field splitting of d-orbitals. Hence, it is concluded that they have the same fused ring structure as the *N*-salicylideneglycinatoaquocopper (II),[6] I, in which the salicylideneglycinate is coordinated around copper(II) as a tridentate ligand.[8]



(I) *N*-Salicylideneglycinatoaquocopper(II)[8]

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[1] G. L. Eichhorn and J. W. Dawes, *J. Am. Chem. Soc.*, **76**, 5663 (1954).

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[3] A. Nakahara, H. Yamamoto and H. Matsumoto, *Sci. Rep., College of General Education, Osaka University*, **12**, 11 (1963).

[4] D. E. Metzler and E. E. Snell, *J. Am. Chem. Soc.*, **74**, 979 (1952).

[5] D. E. Metzler, M. Ikawa and E. E. Snell, *ibid.*, **76**, 648 (1954).

[6] A. Nakahara, This Bulletin, **32**, 1195 (1959)

[7] R. C. Burrows and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **88**, 4150 (1966).

[8] This structure has recently been proved by Professor Masao Kakudo and his co-workers the Institute for Protein Research, Osaka University, by the X-ray crystal analysis.

TABLE 1. ANALYTICAL DATA FOR *N*-SALICYLIDENEAMINO ACID COMPLEXES

Compound*	C,%		H,%		N,%	
	Calcd	Found	Calcd	Found	Calcd	Found
[Cu(salal=D-α-ala)(H_2O)]·2H_2O	38.90	38.41	4.86	5.03	4.54	4.54
[Cu(salal=L-α-ala)(H_2O)]·2H_2O	38.90	38.49	4.86	4.91	4.54	4.53
[Cu(salal=DL-α-ala)(H_2O)]·$\frac{1}{2}H_2O$	42.63	43.22	4.27	4.34	4.98	4.75
[Cu(salal=DL-α-ala)(H_2O)]·H_2O	41.31	40.90	4.47	4.24	4.82	5.05
[Cu(salal=α-AIBA)(H_2O)]	46.07	46.17	4.54	4.48	4.89	4.84
[Cu(salal=L-val)(H_2O)]	47.92	47.70	4.99	5.00	4.66	4.53
[Cu(salal=L-leu)(H_2O)]·$\frac{1}{2}H_2O$	48.15	48.05	5.66	5.56	4.32	4.25
[Cu(salal=L-ileu)(H_2O)]	49.60	49.51	5.41	5.33	4.45	4.39
[Cu(salal=L-phe)(H_2O)]·Salal·H_2O**	56.50	56.32	4.73	4.69	2.88	2.84
[Cu(salal=D-phegly)(H_2O)]·H_2O	51.06	51.03	4.54	4.24	4.26	3.90
[Cu(salal=L-glu)(H_2O)]·2H_2O	39.45	39.39	4.64	4.80	3.82	3.82
[{Cu(salal=L-asp)(H_2O)}$_2$>Cu(H_2O)$_2$]***	36.14	35.95	3.28	3.38	3.83	3.84
[Cu(salal=DL-ser)(H_2O)]·H_2O	39.15	39.46	4.24	4.39	4.56	4.48

* The amino acid moieties are represented as follows: ala=alanine, AIBA=aminoisobutyric acid, val=valine, leu=leucine, ileu=isoleucine, phe=phenylalanine, phegly=phenylglycine, glu=glutamic acid, asp=aspartic acid, ser=serine.

** This compound has an uncoordinated salicylaldehyde of crystallization.

*** The polynuclear type complex as illustrated in II; Cu, 26.1 (Calcd), 25.5 (Found); H_2O, 9.85 (Calcd), 9.42 (Found).

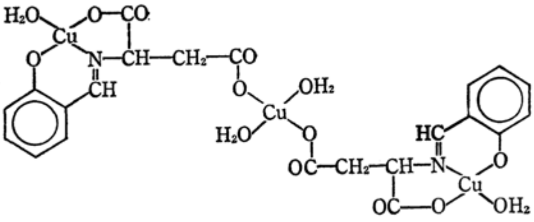
TABLE 2. SOME PROPERTIES OF *N*-SALICYLIDENEAMINO ACID COMPLEXES

Compound*	Appearance of crystals	Decomposing temperature °C	Absorption max., ν_{max} 10^{13}sec^{-1}
[Cu(salal=L-α-ala)(H_2O)]·2H_2O	green plate	219—220	45.5
[Cu(salal=α-AIBA)(H_2O)]	green plate	>300	45.8
[Cu(salal=L-val)(H_2O)]	green needle	226—229	45.5
[Cu(salal=L-leu)(H_2O)]·$^1/_2H_2O$	green needle	205—206	45.5
[Cu(salal=L-ileu)(H_2O)]	green needle	202—210	45.3**
[Cu(salal=L-phe)(H_2O)]·Salal·H_2O	green needle	203—208	45.5**
[Cu(salal=D-phegly)(H_2O)]	green needle	210—215	45.3
[Cu(salal=L-glu)(H_2O)]·2H_2O	green needle	208—213	45.5
[{Cu(salal=L-asp)(H_2O)}$_2$>Cu(H_2O)$_2$]	green plate	191—198	45.2**
[Cu(salal=DL-ser)(H_2O)]·H_2O	green needle	210—215	45.5

* Abbreviations for amino acid moieties are the same as those in Table 1.

** The solvents used were one-to-one volume mixture of water: dimethylsulfoxide.
Unless otherwise specified, the solvent were 1 : 9 (by volume) dimethylsulfoxide: water mixture.

The possibility for the additional coordination of γ-carboxyl group of glutamate-Schiff base complex is excluded not only by the elemental analyses but also by the presence of the CO stretching band in 1720 cm^{-1}, which is characteristic of the uncoordinated carboxyl group. On the other hand the same kind of CO band is not observed in the case of aspartate-Schiff base complex. This suggests the participation of the β-carboxyl group in coordination. Since the results of elemental analyses for this compound, however, indicate that the ratio of copper(II) to Schiff base ligand is 3 : 2, as is clear from Table 1, the structure of aspartate-Schiff base complex in the crystalline state may be a kind of a polynuclear type complex as illustrated below:



(II) Possible structure of the copper(II) chelate of Schiff base derived from salicylaldehyde and aspartate

The proposed structure may be supported by the rather small extinction for one mole copper(II) ion. The log ε per one mole copper(II) of the aspartate-Schiff base chelate was estimated to be 1.91, whereas those of other Schiff base chelates were around 2.05, in the same solvent.

Similarly a question will be arisen on the possibility of the additional coordination of the hydroxyl group in the serine-Schiff base chelate. Since the binding ability of the alcohol oxygen is, however, estimated to be comparatively weak in acid or neutral medium,[3] the hydroxyl group of serine may be free from coordination.

The investigations of amino acid syntheses and transamination reactions by making use of those Schiff base chelates are now under way in this laboratory.

Experimental

Preparations. All the chelates were prepared by the reactions of bis(salicylaldehydato) copper (II) with the respective amino acids in 1 : 1 molar ratio, in water at about 60°C[6]. Since the solubilities of the products in water were comparatively small in all cases, they were easily separated by filtration. Recrystallizations were successfully performed from water or aqueous ethanol (two-to-one by volume). The results of elemental analyses are tabulated in Table 1.

Measurements. The visible and ultraviolet absorption spectra were determined with a Shimadzu Spectrophotometer QR-50 at room temperature. The solvents used in this work were dimethylsulfoxide-water system in all cases, because of their poor solubilities in pure water. Only the numerical data for the absorption maxima in the visible region are listed in Table 2. The infrared spectra were recorded by the use of a Hitachi EPI-2 Infrared Spectrophotometer. The measurements were made at room temperature using the pressed potassium bromide disk technique in the wave-number range from 700 to 4000 cm^{-1}.