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Reactions of Metal Chelates. IV.[1] The Reactions of Bis(salicylaldehydato)copper(II) with Diethylenetriamine and Triethylenetetramine

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The reactions of bis(salicylaldehydato)copper(II) with diethylenetriamine and triethylenetetramine were investigated under several different conditions. In water, in the absence of other reagents, the reactions gave uncharged bis(salicylaldehyde)-diethylenetriamine- and -triethylenetetramine-copper(II), respectively. In the presence of an acid the resulting complexes were the respective cation complexes, in which only one of the two terminal nitrogen atoms was in the form of Schiff base with salicylaldehyde. In the presence of a salt, the resulting complex from diethylenetriamine was a cation complex, and that from triethylenetetramine an uncharged complex. Three new copper(II) chelates were obtained.

It was reported by Sarma and Bailar[2] that bis(salicylaldehydato)copper(II) reacts with triethylenetetramine to give bis(salicylaldehyde)triethylenetetraminecopper(II), (IV), in which the two terminal nitrogen atoms of the original triethylenetetramine molecule link to copper(II) in the form of Schiff base, whereas the other two imine-nitrogen atoms are free from coordination. However, we have recently found that the same reaction, under somewhat modified conditions, produces an entirely different chelate, (V), as indicated in Fig. 1. The reaction of complex (I) with diethylenetriamine (instead of triethylenetetramine) was found to proceed differently according to the conditions. The present paper deals with the results of reactions between bis(salicylaldehydato)copper(II), I, and diethylenetriamine or triethylenetetramine under three different conditions: (1) the reaction in water in the absence of other reagents; (2) the reaction in the presence of various salts such as sodium perchlorate, nitrate, bromide or chloride; (3) the reaction in the presence of some acids such as perchloric, nitric, hydrobromic or hydrochloric acid. In most cases, resulting chelates were isolated. The structures of these complexes have been confirmed from elemental analyses and spectrophotometric measurements. For the systems where isolation of the reaction products was very difficult, the electronic spectra of reaction solutions were measured. The structure of complexes produced in solutions has been concluded also from the spectral data. All the results are schematically presented in Fig. 1.

The Reaction of Bis(salicylaldehydato)copper(II), I, with Diethylenetriamine. The reaction of complex I in water with diethylenetriamine in the absence of other reagents gave an olive-green crystalline powder, whereas the same reaction in the presence of sodium perchlorate, bromide or nitrate gave violet crystals. The olive-green complex was found to have the structure (II) in Fig. 1, by taking into account the results of elemental analyses and the quadri-coordinating character of copper(II) complexes. As is clear from the structural formula, II, the two terminal amino groups of diethylenetriamine link to copper(II) in the form of Schiff base with salicylaldehyde, while the central imine-nitrogen is free from coordination. The complex is, therefore, an uncharged neutral molecule. The absorption maximum for the d-d band of the complex II was observed at 570 mμ.

Inspection of the infrared spectra of the violet crystals obtained from the system containing perchlorate or nitrate reveals the band characteristic of perchlorate or nitrate in the region between 1100 and 1380 cm^{-1} (Fig. 2). An aqueous solution of the violet crystal obtained from the system containing bromide ion gives the white precipitate by the addition of a solution of silver nitrate, which indicates the existence of bromide ion as the external ion of the complex. Thus the structure of these violet chelates has been concluded as III in Fig. 1. The results of elemental analyses of these perchlorate, nitrate and bromide complexes also supported the above conclusion. In the case of the chloride of the same complex, it was necessary to concentrate the reaction solution because of its comparatively high solubility in order to isolate the crystals. The absorption maximum in the visible region of the four violet complexes (chloride, bromide, nitrate and perchlorate) always appears at 570 mμ. In

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[1] Part III of this series of papers: This Bulletin, **42**, 1297 (1969).

[2] B. D. Sarma and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **77**, 5476, (1955).

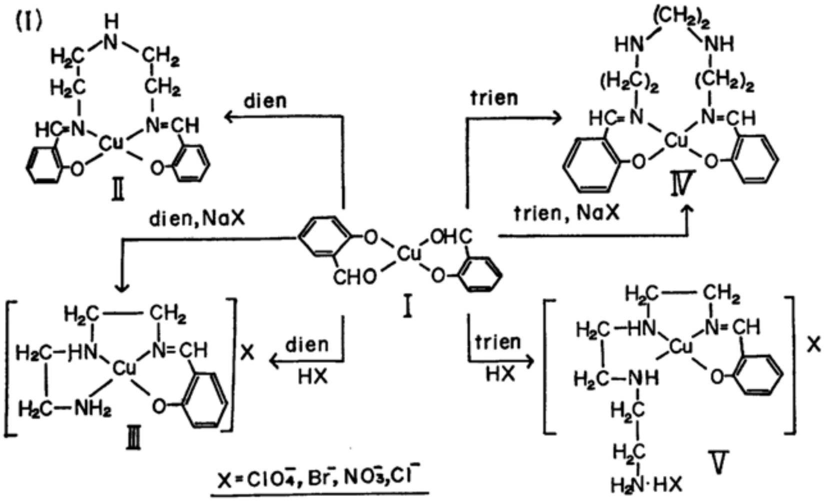

Fig. 1. The Reactions of bis(salicylaldehydato)copper(II) with diethylenetriamine and triethylenetetramine.

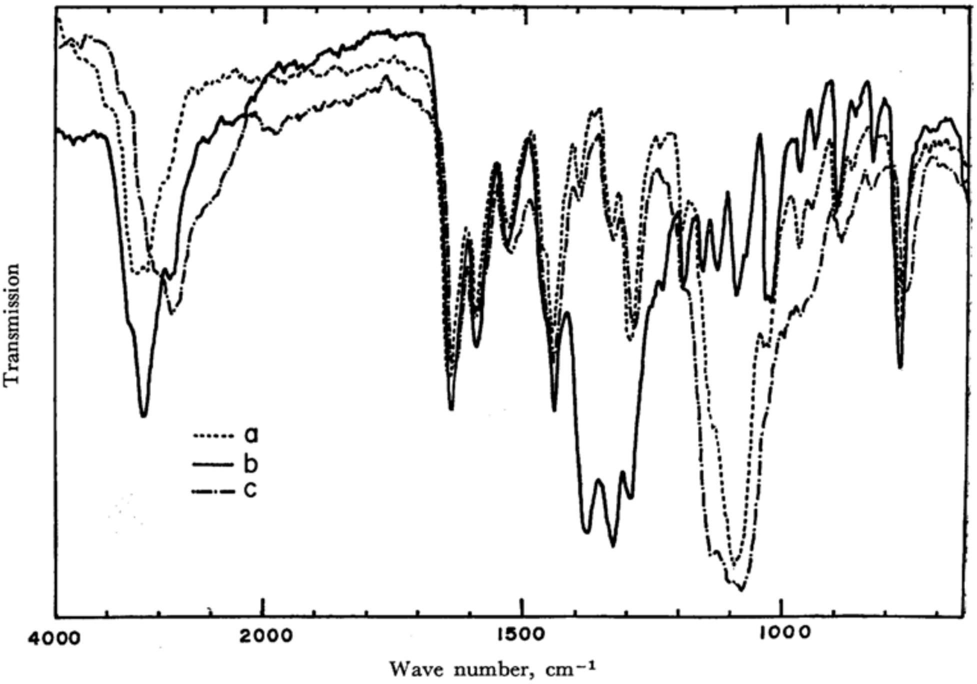

Fig. 2. Infrared spectra of a, [Cu salal=dien]$ClO_4 \cdot H_2O$; b, [Cu salal=dien]$NO_3 \cdot H_2O$; c, [Cu salal=trienH]$(ClO_4)_2$.

spite of their widely different color in the crystalline state, complexes II and III reveal no great difference as far as the d–d band is concerned. However, a considerable difference was observed in the absorption bands in the near ultraviolet region. It is to be noted that chelate III obeys Beer's law even in the concentration of 5×10^{-3} to 5×10^{-5} M, whereas chelate II does not in such a dilute solution. It has been confirmed by infrared study that the resulting chelate from the reaction of complex I with diethylenetriamine in acidic solution is identical with chelate III. These results suggest that the 6-5-5[*1] fused-chelate-ring is so stable that only the presence of some anions favors its formation, instead of the complex of the less stable 6-8-6 fused-chelate-ring structure, II.

[*1] The abbreviation 6-5-5 indicates the fused-chelate-ring structure containing six-, five-, and five-membered ring in counter-clockwise direction.

The Reaction of Bis(salicylaldehydato)copper(II), I, with Triethylenetetramine. In this reaction the product was a bluish green complex, regardless of the absence or presence of salts. As is clear from the structural formula IV, triethylenetetramine is coordinated around copper(II) only through the two terminal nitrogen atoms which are in the form of Schiff base with salicylaldehyde. The complex is, therefore, identical with that reported by Sarma and Bailar[2]. On the other hand, the resulting compound from the reaction in an acidic solution was a cation complex as indicated in (V), in which one terminal amino group was in the form of Schiff base and the other terminal amino nitrogen was in the form of quaternary ammonium salt. Hence the complex has a 6-5-5 fused-chelate-ring structure. The infrared spectrum of the perchlorate of chelate V is shown in Fig. 2. Though the chelate of type V was successfully isolated as perchlorate, its nitrate, bromide or chloride could not be isolated. However, the spectrophotometric investigation of the latter solutions enabled us to conclude the formation of the same type complex cations in each case. In other words, the visible and ultraviolet absorption spectra of these reaction solutions have been disclosed to be more similar to that of V than that of complex IV. Thus in the case of triethylenetetramine, the tendency for producing the 6-5-5 fused-chelate-ring structure seems to be characteristic of the presence of acid, and is in marked contrast with the case of diethylenetriamine. In the latter case, the 6-5-5 fused-chelate-ring structure was produced even by the presence of a neutral salt instead of acids. It is interesting to note that there is a delicate difference between diethylenetriamine and triethylenetetramine in the way of chelate-formation.

Experimental

Bis(salicylaldehydato)copper(II) was prepared according to the direction described in the first paper of this series.[3]

The Preparation of Copper(II) Chelate, II. To a 3.1 g (0.01 mol) of bis(salicylaldehydato)copper(II) in 20 m*l* of water was added 0.9 g (0.01 mol) of diethylenetriamine in 10 m*l* of water. The mixture was stirred at 25°C for about half an hour. After it had been filtered, the solution was evaporated to dryness *in vacuo* to give an olive-green powder. The powder was recrystallized from ethanol containing a small volume of water. Found: C, 55.19; H, 5.05; N, 10.97%. Calcd for $[Cu(C_{18}H_{19}N_3O_2)]\cdot H_2O$: C, 55.31; H, 5.38; N, 10.76%.

The Preparation of the Perchlorate, Nitrate or Bromide of Chelate, III. To a mixture of 0.01 mol each of bis(salicylaldehydato)-copper(II) and diethylenetriamine in 30 m*l* of water was added 0.01 mol of sodium perchlorate, nitrate or bromide. The reaction mixture was stirred at 25°C for about half an hour. After it had been cooled, a small violet crystal was deposited from the solution. This was filtered by suction, and was recrystallized from water. Analytical data of the complexes are given in Table 1.

The Preparation of Chloride of Chelate, III. An almost same procedure as that described above was applied. Since the corresponding violet crystal could not be separated only by allowing the solution to stand, the reaction mixture had to be evaporated to dryness *in vacuo*. The crystalline powder thus obtained was recrystallized from aqueous ethanol. This compound can be prepared by the following method. The mixture of 0.01 mol each of bis-(salicylaldehydato)copper(II), diethylenetriamine and sodium chloride in 30 m*l* of water was adjusted to pH 3—5 by hydrochloric acid. The mixture was stirred at 25°C for half an hour, and a dark blue solution was obtained. After it had been filtered, the filtrate was evaporated to dryness *in vacuo* to give a dark blue powder. Recrystallization of this powder was performed by using aqueous ethanol. The result of elemental analysis is shown in Table 1.

The Reaction between Bis(salicylaldehydato)copper(II) and Diethylenetriamine in Acidic Media. The mixture of 0.01 mol each of bis(salicylaldehydato)copper(II) and diethylenetriamine in 30 m*l* of water was adjusted to pH 3—5 by perchloric, nitric, hydrobromic, or hydrochloric acid. The reaction mixture was stirred at 25°C for half an hour. A violet crystalline product was deposited from the solution except for the case in which hydrochloric acid was used. The crystals were respectively identified as perchlorate, nitrate or bromide of cation complex, III, from their infrared spectra. In the case of chloride of III, visible and ultraviolet absorption spectrum of the reaction solution was measured.

The Preparation of Copper(II) Chelate, IV. Though this compound has already been reported by Sarma and Bailar,[2] a similar procedure as for complex II, was adopted.

The Preparation of the Perchlorate of Chelate, V. The mixture of 0.01 mol each of bis(salicylaldehydato)-copper(II) and triethylenetetramine in 30 m*l* of water

TABLE 1. ANALYTICAL DATA OF [Cu salal=dien]X

Compound	C, %		H, %		N, %	
	Calcd	Found	Calcd	Found	Calcd	Found
[Cu salal=dien]$ClO_4\cdot H_2O$	34.11	34.07	4.65	4.55	10.85	10.37
[Cu salal=dien]$NO_3\cdot H_2O$	37.77	37.94	5.15	5.08	16.02	15.90
[Cu salal=dien]$Br\cdot H_2O$	35.92	36.04	4.90	4.93	11.43	11.38
[Cu salal=dien]$Cl\cdot H_2O$	40.87	40.95	5.57	5.74	13.00	12.43

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3) A. Nakahara, K. Hamada, I. Miyachi and K. Sakurai, This Bulletin, **40**, 2826 (1967).

was adjusted to pH 3—5 by dilute perchloric acid. After it had been stirred at 25°C for about half an hour, the reaction mixture was filtered by suction. A red-violet crystal was deposited, and this was recrystallized from water.

Found: C. 30.65; H, 4.19; N, 10.44 %. Calcd for $[Cu(C_{13}H_{21}N_4OHClO_4)]ClO_4$: C, 30.47; H, 4.30; N, 10.94%.

The Reaction between Bis(salicylaldehydato)-copper(II) and Triethylenetetramine in the Presence of Sodium Perchlorate, Nitrate, Bromide or Chloride. The reactions were carried out in the same way as for chelate III. Each product was identified as the chelate IV from infrared spectrum.

The Reaction between Bis(salicylaldehydato)-copper(II) and Triethylenetetramine in Acidic Media. A similar procedure as for bis(salicylaldehydato)copper(II) with diethylenetriamine in acidic media was adopted. A red-purple crystal was separated only from the system using perchloric acid, but not in the other cases. However, the structure of the complex in each reaction was verified as IV from their absorption spectra.

Measurements

The measurements of visible and ultraviolet absorption spectra were made with a Shimadzu Spectrophotometer QR-50. The infrared spectra were recorded with a Hitachi EPI-2 infrared spectrophotometer. The measurements were carried out at room temperature using the pressed potassium bromide disk technique in the wave number range from 700 to 4000 cm^{-1} with a rock-salt prism.

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