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The Stability of Fused Rings in Metal Chelates. IV. Preparation and Relative Stability of Copper(II) Complexes with Tetradentate Schiff Base Ligands

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Relative stability of sixteen aldehyde- and the corresponding ketone-Schiff base chelates has been investigated in terms of their decomposing temperature and half-wave potential against the reduction of copper(II) at the dropping mercury electrode. The previous conclusion, established for copper(II) tridentate Schiff base complexes, that Schiff base chelates of aldehydes are generally less stable than those of corresponding ketones has been proved to be valid also for copper(II) tetradentate Schiff base complexes if there is no serious steric hindrance in the Schiff base ligand. As a result of this investigation, six new copper(II) chelates were synthesized and characterized.

In a previous paper[1] we have pointed out that copper(II) chelates of aldehyde-Schiff bases are generally less stable than those of the corresponding ketone-Schiff bases. This conclusion was, however, drawn only from the comparison of relative stability of some copper(II) chelates with tridentate Schiff bases derived from glyoxylate or pyruvate and various amino acid residues. The investigation has recently been extended to copper(II) chelates with tetradentate Schiff bases derived from some other aldehydes or ketones and various diamines or glycylglycine. Thus the validity of the former conclusion has been reinvestigated on the basis of experimental data on the relative stability of sixteen copper(II) tetradentate chelates.

The carbonyl compounds employed in this work were not only glyoxylate and pyruvate but also salicylaldehyde, benzoylacetone, benzoylacetaldehyde and 2-hydroxyacetophenone. On the other hand, ethylene-, trimethylene- and tetramethylenediamine, and glycylglycine were employed as amino compounds to form Schiff bases with the above described carbonyl compounds. Structural formulae of the sixteen copper(II) - Schiff base chelates derived from those carbonyl and amino compounds are illustrated in Fig. 1, I—XVI. Among those complexes, I, III, IV, V, VII and XVI are new compounds; the complexes shown by the odd numbers are chelates of aldehyde-Schiff bases,

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[1] Y. Nakao, K. Sakurai and A. Nakahara, This Bulletin, **39**, 1471 (1966).

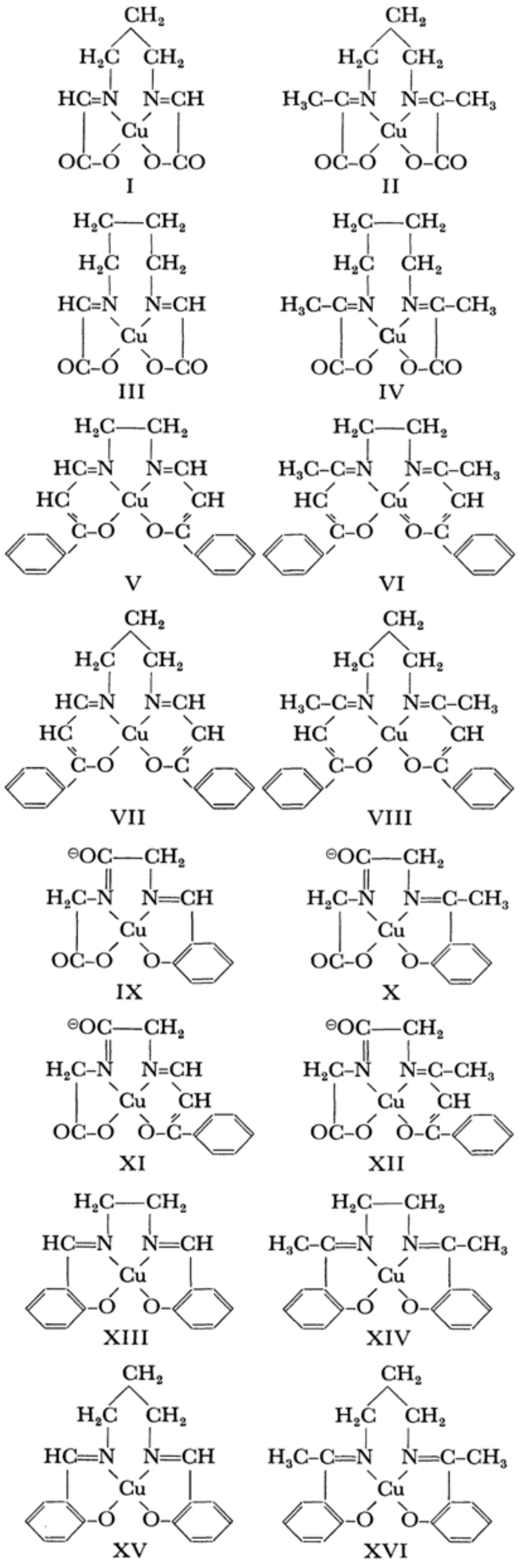

Fig. 1. Structural formulae of copper (II) chelates of aldehyde- and ketone-Schiff bases.

while those shown by the even numbers are of ketone-Schiff bases.

The relative stability of copper(II)-aldehyde- and -ketone-Schiff base complexes has been determined in terms of their decomposing temperature and half-wave potential of the reduction of copper(II) at the dropping mercury electrode.[2] The numerical data are tabulated in Table 1.

Copper(II) Complexes of Schiff Bases derived from Glyoxylate or Pyruvate and Various Diamines (I—IV). The copper(II) complex of Schiff base derived from pyruvate and trimethylenediamine, II, has been reported in a former paper.[2] The corresponding complex of aldehyde-Schiff base derived from glyoxylate and trimethylenediamine, I, has newly been prepared and compared with II. Both of them consist of the same skeletal structure (5-6-5 fused-chelate-ring*1) and are blue crystals, but they distinctly differ from each other in decomposing temperature and half-wave potential of the reduction of copper(II). The numerical data tabulated in Table 1 apparently support the previous conclusion that aldehyde-Schiff base complex is less stable than the corresponding ketone-Schiff base complex. The same trend is also observed in the comparison of bis-(glyoxylate)- and bis(pyruvate)-tetramethylenediamine complex, III and IV, in which the fused-chelate-ring is 5-7-5.

Further it may be concluded from the comparison of I and III, or II and IV, that if the carbonyl moiety in Schiff base ligand is same, 5-6-5 fused ring system is more stable than 5-7-5 system. (I$<$II; III$<$IV; I$>$III*2; II$>$IV).

Copper(II) Complexes of Schiff Bases derived from Benzoylacetaldehyde or -acetone and Ethylene- or Trimethylene-diamine (V—VIII). The copper(II) chelates of Schiff base derived from benzoylacetone and ethylenediamine, VI, and that from benzoylacetone and trimethylenediamine, VIII, were reported by Martell *et al.*[3] In the present investigation we have newly prepared the corresponding chelates of aldehyde-Schiff bases, V and VII. As is clear from Table 1, the Schiff base complexes of ethylenediamine, V and VI, are reddish brown, whereas those of trimethylenediamine, VII and VIII, are greenish brown. The

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

2) A. Nakahara, H. Yamamoto and H. Matsumoto, This Bulletin, **37**, 1137 (1964).

[*2] Though this particular relation, I$>$III, does not seem to be decisive because of the fact that the decomposing temperature of the complex I is rather lower than that of the complex III, the conclusion might be supported from the comparison of strain in the fused ring system of the respective chelates.

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

TABLE 1. SOME PROPERTIES OF COPPER(II) CHELATES OF ALDEHYDE- AND KETONE-SCHIFF BASES

Chelate	Ligand (Schiff base)	Color of crystals	Melting (or decomposing) temp. °C	Half-wave potential, $E_{1/2}$ *vs.* SCE at 25°C
I	2 : 1 glyoxylate : trimethylenediamine	blue	190—200 (decomp.)	−0.25 V (irrev.)
II	2 : 1 pyruvate : trimethylenediamine	blue	209—219 (decomp.)	−0.49 V (irrev.)
III	2 : 1 glyoxylate : tetramethylenediamine	pale-blue	200—206 (decomp.)	−0.11 V (irrev.)
IV	2 : 1 pyruvate : tetramethylenediamine	pale-blue	207—215 (decomp.)	−0.34 V (irrev.)
V	2 : 1 benzoylacetaldehyde : ethylenediamine	red-brown	227—229 (decomp.)	−0.87 V (irrev.) (50% H_2O-pyridine)
VI	2 : 1 benzoylacetone : ethylenediamine	red-brown	277—281	−0.90 V (irrev.) (50% H_2O-pyridine)
VII	2 : 1 benzoylacetaldehyde : trimethylenediamine	green-brown	153—154 (decomp.)	−0.70 V (irrev.) (50% H_2O-pyridine)
VIII	2 : 1 benzoylacetone : trimethylenediamine	green	194—196 (decomp.)	$E^{(1)}_{1/2}$, −0.52 V (irrev.) $E^{(2)}_{1/2}$, −0.70 V (irrev.) (50% H_2O-pyridine)
IX	1 : 1 salicylaldehyde : glycylglycine	violet	289 (decomp.)	−0.58 V (irrev.)
X	1 : 1 2-hydroxyacetophenone : glycylglycine	violet	326—330 (decomp.)	−0.67 V (irrev.)
XI	1 : 1 benzoylacetaldehyde : glycylglycine	violet	222—225 (decomp.)	−0.60 V (irrev.)
XII	1 : 1 benzoylacetone : glycylglycine	violet	244—246 (decomp.)	−0.68 V (irrev.)
XIII	2 : 1 salicylaldehyde : ethylenediamine	green	276—285 (decomp.)	−0.75 V (irrev.) (50% H_2O-pyridine)
XIV	2 : 1 2-hydroxyacetophenone : ethylenediamine	red-brown	235—242 (decomp.)	−0.63 V (irrev.) (50% H_2O-pyridine)
XV	2 : 1 salicylaldehyde : trimethylenediamine	green-brown	276—280 (decomp.)	−0.53 V (irrev.) (50% H_2O-pyridine)
XVI	2 : 1 2-hydroxyacetophenone : trimethylenediamine	green	242—247 (decomp.)	−0.49 V (irrev.) (50% H_2O-pyridine)

extraordinary difference is also found in their decomposing temperature and half-wave potential. It is noteworthy that even this kind of distinct difference is accompanied by the slight change of fused ring from the 6-5-6 to 6-6-6 system.

The aldehyde-Schiff base complexes are proved, also here, to be less stable than the corresponding ketone-Schiff base complexes; in the comparison of the same two aldehyde-Schiff base chelates, or ketone-Schiff base chelates, the stability of the 6-5-6 fused ring structure is higher than that of the 6-6-6 structure. (V<VI; VII<VIII; V>VII; VI>VIII).

Copper(II) Complexes of Schiff Bases with Glycylglycine (IX—XII). As already reported,[4] copper(II) chelates of Schiff bases derived from salicylaldehyde, 2-hydroxyacetophenone, benzoylacetaldehyde or benzoylacetone and glycylglycine have the structure of 5-5-6 fused ring and appear reddish purple. Thier decomposing temperature and half-wave potential in polarographic measurement are indicated in Table 1, from which the following relation in their relative stability is easily concluded: IX<X; XI<XII. The validity of the previous conclusion that Schiff base chelates of aldehydes are less stable than those of ketones is thus well supported.

Copper(II) Complexes of Schiff Bases derived from Salicylaldehyde or 2-Hydroxyacetophenone and Ethylene- or Trimethylenediamine (XIII—XVI). Bis(salicylaldehyde)-ethylenediimine chelate, XIII, -trimethylenediimine chelate, XV, and bis(2-hydroxyacetophenone)ethylenediimine chelate, XIV, have long been known since the work of Tsumaki *et al.*[5] In addition to those, we have newly prepared bis(2-hydroxyacetophenone)trimethylenediimine chelate, XVI.

Inspection of the numerical data for these chelates in Table 1 reveals that the situation on relative stability of aldehyde- and ketone-Schiff base chelates is the reverse of the cases described above. In other words, the Schiff base complexes of aldehydes are more stable than those of ketone, so far as these particular chelates are concerned. However, the reversal of this kind may be attributed to a steric hindrance resulting from the bulky methyl group of the 2-hydroxyacetophenone moiety. The steric effect of the methyl group can easily be duplicated by using a Stuart Model. Although this effect of methyl group does not seem to be so serious, but still it may be great enough to weaken the coordination of the tetradentate ligand to some extent. For this reason, it may be understood that the ketone Schiff base chelates, XIV and XVI,

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

5) P. Pfeiffer, E. Breith, E. Lübbe and T. Tsumaki, *Ann.*, **503**, 84 (1933).

become less stable than the aldehyde-Schiff base chelates, XIII and XV. In the case of complex X, in which the Schiff base ligand consists of glycylglycine and 2-hydroxyacetophenone, the steric hindrance of the same methyl group has not been necessary to be taken into account. This is because of the reason that the complex X contains only one 2-hydroxyacetophenone moiety in the molecule, and hence the steric effect of methyl group is considered to be not so serious as that in complexes, XIV or XVI.

Thus the previous conclusion that Schiff base chelates of aldehydes are generally less stable than those of corresponding ketones is proved to be valid also for tetradentate chelates, whenever there is no serious steric hindrance in the ligand.

Experimental

Syntheses of Ligands. *Sodium Glyoxylate* was prepared from tartaric acid according to the direction of Metzler *et al.*[6]

Benzoylacetaldehyde was prepared from acetophenone according to the direction in the literature.[7]

Bis(benzoylacetaldehyde)ethylendiimine. To a mixture of 5.2 g of benzoylacetaldehyde and 0.8 g of sodium hydroxide in 80 m*l* of ethanol was added 2.4 g of ethylenediamine dihydrochloride. The mixture was stirred and heated at about 55°C for several hours, and was then filtered. The filtrate was concentrated to some extent and allowed to stand for a few hours in a refrigerator; thereupon yellow crystals were deposited. The product was filtered and recrystallized from ethanol. Mp 143—144°C. Found: C, 74.99; H, 6.17; N, 8.64%. Calcd for $C_{20}H_{20}O_2N_2$: C, 75.00; H, 6.26; N, 8.75%.

Bis(2-hydroxyacetophenone)trimethylenediimine. A mixture of 5.9 g of 2-hydroxyacetophenone and 1.6 g of trimethylenediamine was dissolved in 10 m*l* of ethanol. The mixture was stirred and heated at about 70°C for half an hour. Upon cooling the solution yellow crystals were deposited. This was filtered and recrystallized from ethanol. Mp 127°C. Found: C, 73.17; H, 7.01; N, 8.81%. Calcd for $C_{19}H_{22}O_2N_2$: C, 73.55; H, 7.10; N, 9.03%.

Preparation of Metal Chelates. *Copper(II) Complex of Bis(glyoxylate)trimethylenediimine(I).* To a mixture of 1.8 g of trimethylenediamine and 5.7 g of sodium glyoxylate in 10 m*l* of water was added a freshly precipitated cupric oxide (*ca.* 2 g). The mixture was vigorously stirred at 10°C for about four hours; hereupon a bluish crystalline powder was gradually deposited. This was recrystallized from water. Found: C, 30.25; H, 4.19; N, 10.32%. Calcd for $Cu(C_7H_8O_4N_2)\cdot 1.5H_2O$: C, 30.60; H, 4.01; N, 10.20%.

Copper(II) Complex of Bis(pyruvate)trimethylenediimine(II). Although the method of preparation of this compound had already been reported in the previous paper,[2] the procedure was a little simplified by the use of copper(II) acetate in place of freshly precipitated copper(II) oxide.

Copper(II) Complex of Bis(glyoxylate)tetramethylenediimine (III). To a mixture of 2.2 g of tetramethylenediamine and 5.7 g of sodium glyoxylate monohydrate in 50 m*l* of water was added 5.0 g of copper(II) acetate monohydrate. The mixture was stirred at 20°C for one hour to give a pale blue crystalline powder. This was filtered and washed several times by water. Found: C, 29.79; H, 5.12; N, 8.30%. Calcd for $Cu(C_8H_{10}O_4N_2)\cdot 3.5H_2O$: C, 29.58; H, 5.24; N, 8.62 %.

Copper(II) Complex of Bis(pyruvate)tetramethylenediimine (IV). To a freshly precipitated cupric oxide, obtained from 10 g of copper(II) sulfate pentahydrate in 50 m*l* of water was added 4.4 g of pyruvic acid and 2.2 g of tetramethylenediamine. The mixture was stirred and heated at 40°C for about two hours. After it had been filtered, the solution was, to some extent, evaporated *in vacuo*, and then allowed to stand for a few hours in a refrigerator; hereupon a blue powder was deposited. This was filtered and recrystallized from water. Found: C, 34.93; H, 6.07; N, 8.05%. Calcd for $Cu(C_{10}H_{14}O_4N_2)\cdot 3H_2O$: C, 34.93; H, 5.82; N, 8.17%.

Bisbenzoylacetaldehyde-ethylenediiminocopper(II) (V). To a mixture of 2.2 g of bis(benzoylacetaldehyde)ethylenediimine and 35 m*l* of acetone was added a freshly precipitated copper(II) oxide obtained from 4.0 g of copper(II) sulfate pentahydrate. The mixture was stirred and heated at 60°C for about three hours. After it had been filtered, the solution was cooled to give reddish brown crystals. This was recrystallized from acetone. Found: C, 62.76; H, 4.58; N, 7.31%. Calcd for $Cu(C_{20}H_{18}O_2N_2)$: C, 62.91; H, 4.72; N, 7.34%.

Bisbenzoylacetone-ethylenediiminocopper(II) (VI) and Bisbenzoylacetone-trimethylenediiminocopper(II) (VIII), were prepared according to the method of Martell *et al.*[3]

Bisbenzoylacetaldehyde-trimethylenediiminocopper(II) (VII). Seven grams of benzoylacetaldehyde, 1 g of sodium hydroxide and 3.4 g of trimethylenediamine dihydrochloride were mixed together in 80 m*l* of ethanol. The mixture was stirred and heated at 60°C for three hours. After it had been filtered, the solution was concentrated under vacuum until the volume became to about 20 m*l*. To this solution of bisbenzoylacetaldehyde-trimethylenediimine was added copper(II) oxide, which had been obtained from 10 g of copper(II) sulfate pentahydrate, and 50 m*l* of acetone. The copper(II) chelate, VII, was thus obtained and purified according to the same procedure as described for the preparation of the chelate V. Found: C, 64.19; H, 5.06; N, 6.95%. Calcd for $Cu(C_{21}H_{20}O_2N_2)$: C, 63.72; H, 5.06; N, 7.08%.

Copper(II) Chelates of Glycylglycine-Schiff Bases (IX–XII). The preparation of these chelates were already reported.[4]

Bissalicylaldehyde-ethylenediiminocopper(II) (XIII), Bis-2-hydroxyacetophenone-ethylenediiminocopper(II) (XIV), and Bissalicylaldehyde-trimethylenediiminocopper(II) (XV), were prepared according to the method of Tsumaki *et al.*[5]

Bis-2-hydroxyacetophenone-trimethylenediiminocopper (II) (XVI). Two grams of bis-2-hydroxyacetophenone-trimethylenediimine was dissolved in 40 m*l* of acetone, and was mixed together with freshly precipitated copper(II) oxide, which had been obtained from 4.0 g of copper(II) sulfate pentahydrate. The mixture was stirred and heated at 60°C for four hours. After it had been filtered, the solution was cooled to give green crystals. This was recrystallized from acetone. Found: C, 61.61; H, 5.48; N, 7.56%. Calcd for $Cu(C_{19}H_{20}O_2N_2)$: C, 61.37; H, 5.38; N, 7.54%.

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[6] D. E. Metzler, J. Olivard and E. E. Snell, *J. Am. Chem. Soc.*, **76**, 647 (1954).

[7] Org. Reaction, Vol VIII, p. 126.

Polarographic Measurements. The measurements were carried out by the same method as already described.[1] The solvent used was water for the compounds I—IV and IX—XII, and 50% (by volume) pyridine-water for V—VIII and XIII—XVI.

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