The Addition Compounds of Bis-Salicylaldehyde Copper(II) and its Derivatives with Pyridine, and α, α'-Dipyridyl

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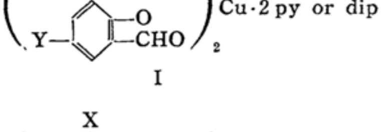
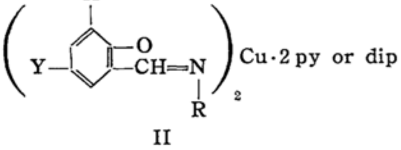
Recently, a few compounds have been reported in which the copper(II) atom appears to be five-coordinate[1] or six-coordinate[2] in the solid state, although the copper(II) ion is normally reluctant to raise its coordination number of four. On the other hand, it is well known that inner complexes of four-coordinated nickel (II) add two molecules of pyridine to form six-coordinated nickel(II) complexes[3-5]. For example, bis-pyridine-bis-salicylaldehyde nickel(II) was isolated crystalline from pyridine solution of bis-salicylaldehyde nickel(II)[5]. Therefore, it is interesting to see whether or not inner complexes of four-coordinated copper(II) form addition compounds with pyridine in a similar manner to nickel(II) complexes. Also, α, α'-dipyridyl presumably forms a more stable coordination compound than does pyridine, because chelation greatly enhances coordination. Accordingly, the present writer has undertaken to examine whether bis-salicylaldehyde copper(II) and its derivatives form addition compounds with pyridine or α, α'-dipyridyl. In several instances, it was possible to isolate well-defined crystalline compounds containing two molecules of pyridine or one molecule of α, α'-dipyridyl having formula I.



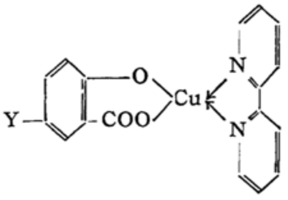
I



II

(X: H, NO_2; Y: H, Br, NO_2; py: Pyridine; dip: α, α'-Dipyridyl; R: C_6H_5, $CH_3C_6H_4$).

They are soluble in organic solvents and insoluble in water, except α, α'-dipyridyl-3-nitrosalicylaldehyde copper(II). All of the addition compounds with pyridine lost the pyridine on heating in ethanol or in benzene, leading to the precipitation of bis-salicylaldehyde copper(II) or its derivatives, while several addition compounds with α, α'-dipyridyl produced α, α'-dipyridyl-copper(II)-mono-salicylate and its derivatives (formula III) on heating their ethanolic or pyridine solutions. The above result showed that the aldehyde group was oxidized to a carboxyl group.



III

(Y: H, Cl, Br, NO_2.)

Further, it was possible to isolate several addition compounds of substituted bis-salicylaldimine complexes of copper(II) with pyridine or α, α'-dipyridyl (formula II). They lost pyridine or α, α'-dipyridyl on heating in organic solvents.

An analogous addition reaction has been reported by Dwyer[6] who found that bis-diazoaminobenzene copper(II) added two molecules of pyridine or one molecule of ethylenediamine. Ley and Wingner[7] found that bis-glycine copper(II) added two molecules of ammonia. These investigators considered that the chelate rings were broken and these addition compounds of copper(II) were four-coordinate[6,8]*.

There are studies by several investigators that copper(II) can form complexes with

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[1] D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, **1956**, 594.

[2] S. Kirschner, *J. Am. Chem. Soc.*, **78**, 2372 (1956).

[3] P. Pfeiffer, E. Bucholtz and O. Bauer, *J. prakt. Chem.*, **129**, 63 (1931).

[4] F. P. Dwyer and D. P. Meller, *J. Am. Chem. Soc.*, **63**, 81 (1941).

[5] F. Basolo and W. R. Matoush, ibid., **75**, 5663 (1953).

[6] F. P. Dwyer, ibid. **63**, 78 (1941).

[7] H. Ley and G. Wingner, *Z. Electrochemie.*, **11**, 584 (1905).

[8] H. Ley, *Ber.*, **42**, 354 (1909).

coordination number higher than four[9]. Recently Kirschner[2] has shown by infrared and rotatory dispersion studies that copper(II) ethylenediaminetetra-acetate and copper(II) bis-aspartate are six-coordinate. Although these addition compounds of copper(II) studied in the present report may be six-coordinate, it seems more likely that they are four-coordinate in view of the comparative rarity of copper(II) complexes with a higher coordination number and the lack of experimental data on these addition compounds by physical means such as infrared spectroscopy.

Experimental

(A) Preparation of bis-salicylaldehyde copper(II) and its derivatives.—These complexes were obtained by the addition of aqueous solution of cupric acetate to the ethanolic solution of salicylaldehyde or its derivatives in the usual way as reported in the literature.

(B) Preparation of addition compounds with pyridine.—They were obtained by dissolving complexes prepared in (A) in cold pyridine and by precipitating with cold water. They were purified by recrystallization from pyridine. Bis-5-chlorosalicylaldehyde copper(II) and bis-5-bromosalicylaldehyde copper(II) did not form addition compounds with pyridine.

1. *Bis-pyridine-bis-5-bromo-3-nitrosalicylaldehyde copper(II)*.—Light green prismatic crystals which loss pyridine at about 110°C.

Anal. Found: C. 40.64; H, 2.52; N, 8.15; Cu, 8.74; pyridine, 22.31. Calcd. for $C_{14}H_6O_8N_2Br_2Cu\cdot 2C_5H_5N$: C, 40.50; H, 2.27; N, 7.87; Cu, 8.93; pyridine 22.23%.

2. *Bis-pyridine-bis-3-nitrosalicylaldehyde copper (II)*. Yellow green prismatic crystals which loss pyridine at about $90^\circ\sim100^\circ$C.

Anal. Found: N, 10.38; Cu, 11.24; pyridine, 28.46. Calcd. for $C_{14}H_8O_8N_2Cu\cdot 2C_5H_5N$: N, 10.12; Cu, 11.47; pyridine, 28.56%.

3. *Bis-pyridine-bis-5-nitrosalicylaldehyde copper (II)*.—Deep green prismatic crystals which loss pyridine slowly at about $40^\circ\sim50^\circ$C.

Anal. Found: N, 10.13; Cu, 11.25; pyridine, 28.15. Calcd. for $C_{14}H_8O_8N_2Cu\cdot 2C_5H_5N$: N, 10.12; Cu, 11.47; pyridine, 28.56%.

4. *Bis-pyridine-bis-salicylaldehyde copper (II)*.—Light green prismatic crystals which loss pyridine slowly at room temperature. Therefore, the analysis was performed without delay after preparation.

Anal. Found: N, 5.93; Cu, 13.72; pyridine, 33.87. Calcd. for $C_{14}H_{10}O_4Cu\cdot 2C_5H_5N$: N, 6.09; Cu, 13.82; pyridine, 34.10%.

5. *Bis-pyridine-bis-salicylal-aniline copper (II)*.—Light green prismatic crystals which lose pyridine slowly at room temperature.

Anal. Found: N, 9.20; Cu, 10.36; pyridine, 25.58. Calcd. for $C_{26}H_{20}O_2N_2Cu\cdot 2C_5H_5N$: N, 9.12; Cu, 10.34; pyridine, 25.76%.

6. *Bis-pyridine-bis-5-bromo-3-nitrosalicylal-toluidine copper (II)*.—Green prismatic crystals.

Anal. Found: N, 9.18; Cu, 7.18; pyridine, 17.67. Calcd. for $C_{28}H_{20}O_6N_4Br_2Cu\cdot 2C_5H_5N$: N, 9.44; Cu, 7.14; pyridine, 17.77%.

(C) Preparation of addition compounds with α, α'-dipyridyl.—The addition compounds with α, α'-dipyridyl were obtained by dissolving the calculated amount of α, α'-dipyridyl and complexes prepared in (A) in cold pyridine or in ethanol and by precipitating with cold water. They were purified by recrystallization from pyridine without heating. Bis-5-chlorosalicylaldehyde copper(II) did not form an addition compound and readily gave an oxidized compound directly.

1. *α, α'-Dipyridyl-bis-salicylaldehyde Cu(II)*.—Brown prismatic crystals. This compound was decomposed with dilute sulfuric acid and then subjected to steam distillation. Salicylaldehyde in the distillate was identified by its 2, 4-dinitrophenylhydrazone which melted at $247^\circ\sim248^\circ$C.

Anal. Found: C, 40.70; H, 2.12; N, 6.03; Cu, 13.81. Calcd. for $C_{14}H_{10}O_4Cu\cdot C_{10}H_8N_2$: C, 40.61; H, 1.99; N, 6.07; Cu, 13.75%.

2. *α, α'-Dipyridyl-bis-5-bromosalicylaldehyde copper (II)*.—Greenish yellow prismatic crystals.

Anal. Found: N, 4.61; Cu, 10.03, Calcd, for $C_{14}H_8O_4Br_2Cu\cdot C_{10}H_8N_2$: N, 4.52; Cu, 10.25%.

3. *α, α'-Dipyridyl-bis-5-nitrosalicylaldehyde copper(II)*.—*Light green prismatic crystals.*

Anal. Found: N, 10.27; Cu, 11.73. Calcd. for $C_{14}H_8O_8N_2Cu\cdot C_{10}H_8N_2$: N, 10.15; Cu, 11.51%.

4. *α, α'-Dipyridyl-bis-5-bromo-3-nitrosalicylaldehyde copper(II)*.—Yellow-green prismatic crystals. When this complex was decomposed by dilute sulfuric acid and the solution was extracted with ether, light yellow needle crystals of 5-bromo-3-nitrosalicyaldehyde melting at $147^\circ\sim148^\circ$C were obtained.

Anal. Found: N, 8.05, Cu, 8.88. Calcd. for $C_{14}H_6O_8N_2Br_2Cu\cdot C_{10}H_8N_2$: N, 7.90; Cu 8.95%.

5. *α, α'-Dipyridyl-bis-3-nitrosalicylaldehyde copper (II)*.—Yellow-brown crystals. This complex was insoluble in alcohol, but was soluble in cold water to a certain extent. It could not be oxidized.

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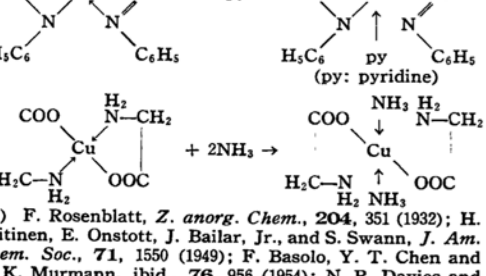

[9] F. Rosenblatt, *Z. anorg. Chem.*, **204**, 351 (1932); H. Laitinen, E. Onstott, J. Bailar, Jr., and S. Swann, *J. Am. Chem. Soc.*, **71**, 1550 (1949); F. Basolo, Y. T. Chen and R. K. Murmann, ibid., **76**, 956 (1954); N. R. Davies and F. P. Dwyer, *J. Proc. Roy. Soc. N. S. W.*, **86**, 64 (1954) etc.

Anal. Found: N, 10.16; Cu, 11.36. Calcd. for $C_{14}H_8O_8N_2Cu \cdot C_{10}H_8N_2$: N, 10.15; Cu, 11.51%.

6. α, α'-Dipyridyl-bis-salicylal-aniline copper (II).—Green prismatic crystals.

Anal. Found: N, 9.31; Cu, 10.44. Calcd. for $C_{26}H_{20}O_2N_2Cu \cdot C_{10}H_8N_2$: N, 9.15; Cu, 10.38%.

7. α, α'-Dipyridyl-bis-5-bromo-3-nitrosalicylal-aniline copper (II).—Red-brown prismatic crystals.

Anal. Found: N, 9.67; Cu, 7.52. Calcd. for $C_{26}H_{16}O_6N_4Br_2Cu \cdot C_{10}H_8N_2$: N, 9.77; Cu, 7.39%.

(D) Oxidation of α, α'-dipyridyl complexes.—When the addition compounds with α, α'-dipyridyl were dissolved in ethanol or pyridine, heated on a water bath for about half an hour, and precipitated with water, gray needles of α, α'-dipyridyl copper(II)-monosalicylate and its derivatives were obtained. The pure complexes were obtained by recrystallization from ethanol. When these complexes were decomposed with dilute sulfuric acid and were distilled in steam or extracted with ether, salicylic acid and its derivatives were obtained, and α, α'-dipyridyl-copper (II)-sulfate was isolated from the residue.

1. α, α'-Dipyridyl-copper(II)-monosalicylate.—Gray needles which melt at 262°∼263°C with decomposition.

Anal. (the sample obtained by oxidation) Found: C, 53.16; H, 4.06; N, 7.46; Cu, 16.83. Calcd. for $C_7H_4O_3Cu \cdot C_{10}H_8N_2 \cdot 1.5\ H_2O$: C, 53.33; H, 3.95; N, 7.32; Cu, 16.60%.

The complex obtained by heating a calculated amount of copper(II)-monosalicylate and α, α'-dipyridyl in ethanol, showed nearly the same m. p. (262°∼263°C) and analytical result as the complex obtained by oxidation of α, α'-dipyridyl-bis-salicylaldehyde copper(II). Therefore, it was concluded that the structure of this compound corresponded to the formula III.

Anal. Found: N, 7.59; Cu, 16.77%.

2. α, α'-Dipyridyl-copper(II)-mono-5-bromosalicylate.—Green needles.

Anal. Found: N, 5.85; Cu, 13.79; H_2O, 7.48. Calcd. for $C_7H_3O_3BrCu \cdot C_{10}H_8N_2 \cdot 2H_2O$: N, 6.08; Cu, 13.36; H_2O, 7.61%.

3. α, α'-Dipyridyl-copper(II)-mono-5-nitrosalicylate.—Gray needles.

Anal. Found: N, 10.36; Cu, 15.84. Calcd. for $C_7H_3O_5N \cdot Cu \cdot C_{10}H_8N_2$: N, 10.48; Cu, 15.85%.

4. α, α'-Dipyridyl-copper(II)-mono-5-chlorosalicylate.—Gray needles.

Anal. Found: N, 6.88; Cu, 14.76; H_2O, 8.50. Calcd. for $C_7H_3O_3ClCu \cdot C_{10}H_8N_2 \cdot 2H_2O$: N, 6.64; Cu, 14.90; H_2O, 8.41%.

5. Oxidation product of α, α'-dipyridyl-bis-5-bromo-3-nitrosalicylaldehyde copper(II).—When the complex which was obtained by oxidation of α, α'-dipyridyl-bis-5-bromo-3-nitrosalicylaldehyde copper(II) was decomposed with dilute sulfuric acid and the decomposition product was extracted with ether, white needle crystals were obtained. When this compound was recrystallized from dilute sulfuric acid, colorless needle crystals melting at 216.5°∼217.5°C were obtained. This compound was not 5-bromo-3-nitrosalicylic acid or its aldehyde, and its constitution is not yet elucidated.

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