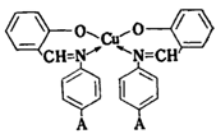
Some Addition Compounds of Salicylaldehyde-ethylenediimine-copper. IV.*

By Tsuguo TANAKA

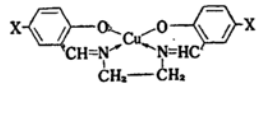
(Received August 17, 1959)

Recently, some observation have been reported[1] about the influence of substituents in the ligand molecules on the physical and chemical properties of their metal chelates. Calvin et al.[2] presented the following order about the stability of the chelates, which he explained on the basis of mesomeric effect, among the substituents A in a metal chelate of salicylaldehyde-anil (I) by the measurement of their half wave potential.

$$OCH_3 > OH > CH_3 > H > C_6H_5 > SO_3Na > NO_2$$



(I)



(II)

An analogous but not identical order of substituents was also observed by the present author[3] about the tendency of the formation of the addition compounds of 5,5′-disubstituted salicylaldehyde-ethylenediimine-copper (II) with propionic acid, phenol and chloroform; the order was

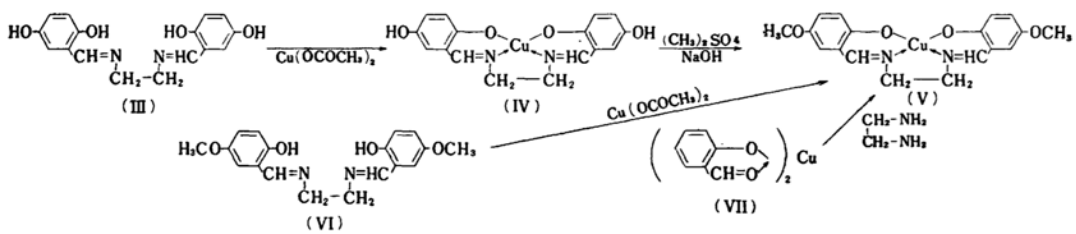
$$5,5'\text{-}CH_3 > 5,5'\text{-}H > 5,5'\text{-}NO_2 > 5,5'\text{-}Cl$$

Now, it was attempted to obtain a further illustration about the influence of the 5,5′-substituent groups in salicylaldehyde-ethylenediimine-copper on the formation of the addition compounds.

5,5′-Dibromo-, 5,5′-diiodo- and 5,5′-dimethoxy-salicylaldehyde-ethylenediimine-copper were synthesized according to the usual procedure[3,4]. 5,5′-Dibromosalicylaldehyde-ethylenediimine-copper was obtained as a purple addition compound with chloroform when it was recrystallized from chloroform, which was eliminated on standing in the air to give a pure green 5,5′-dibromo-salicylaldehyde-ethylenediimine-copper.

The metal chelate which was obtained by the reaction of 5-iodosalicylaldehyde-copper with ethylenediamine-monohydrate in an ethanolic solution was a purple addition compound of 5,5′-diiodosalicylaldehyde-ethylenediimine-copper with ethanol which lost ethanol, when heated at 110°C for thirty minutes, to give dark green 5,5′-diiodosalicylaldehyde-ethylenediimine-copper. Free 5,5′-diiodosalicylaldehyde-ethylenediimine-copper formed addition compounds with ethanol and chloroform.

But the reaction of 5-hydroxysalicylaldehyde with copper acetate in an ethanolic solution resulted in the formation of a black polymeric copper salt, which could not be converted into 5,5′-dihydroxysalicylaldehyde-ethylenediimine-copper by a reaction with ethylenediamine in ethanol. Therefore, 5-hydroxysalicylaldehyde was treated with ethylenediamine-monohydrate in an ethanol to give 5,5′-dihydroxysalicylaldehyde-ethylenediimine (III), which on warming in ethanol with an aqueous solution of copper acetate produced dark blue crystals of the copper salt (IV)[5]. The structure of 5,5′-dihydroxysalicylaldehyde-ethylenediimine-copper (IV) was



(III) (IV) (V) (VI) (VII)

* Bis-salicylaldehyde-ethylenediimine-copper.

1) M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945). L. G. G. van Uitert, W. C. Fernelius and B. E. Douglas, ibid., **75**, 457 (1953).

2) M. Calvin and R. H. Bailes, ibid., **68**, 953 (1946).

3) T. Tanaka, ibid., **80**, 4108 (1958).

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

5) C. S. Marvel and N. Tarkoy, *J. Am. Chem. Soc.*, **80**, 832 (1958).

TABLE I. ADDITION COMPOUNDS OF SALICYLALDEHYDE-ETHYLENEDIIMINE-COPPER DERIVATIVES

Substituents	Color of complex	Addition compounds Color (time required for formation, min.)			
		Propionic acid	Phenol	Chloroform	Ethanol
5,5'-OCH_3[a]	yellow green	purple brown (2)	purple (0.5)	—	—
5,5'-I	dark green	purple (6)	purple (0.5)	purple (0.5)	purple[b]
5,5'-OH[a]	gray green	—	purple brown (0.5)	—	—
5,5'-Br	green	—	purple (0.5)	purple[b]	—

a) Powdered sample. b) Recrystallization.

confirmed by the following synthesis.

5,5'-Dihydroxysalicylaldehyde-ethylenediimine-copper (IV) was methylated by treating it with dimethylsulfate and aqueous sodium hydroxide[6], when 5,5'-dimethoxysalicylaldehyde-ethylenediimine-copper (V) was obtained. V was also obtained either by the reaction of 5,5'-dimethoxysalicylaldehyde-ethylenediimine (VI) with an aqueous solution of copper acetate in ethanolic solution, or by the reaction of 5-methoxysalicylaldehyde-copper (VII) with ethylenediamine-monohydrate. Identity of these products was proved by the observation of the absorption spectra.

The formation of the addition compounds of these metal chelates with propionic acid, phenol, chloroform and ethanol was examined and the results were summarized in Table I.

Peculiar behavior of 5,5'-diiodosalicylaldehyde-ethylenediimine-copper was noted; it formed addition compounds with propionic acid as well as with chloroform and ethanol in contrast to other derivatives.

Comparing these results with those already reported, the tendency of the formation of addition compounds is in the following order,

$$\underset{(+)}{5,5'\text{-}CH_3} > \underset{(-)}{5,5'\text{-}OCH_3} > \underset{(-)}{5,5'\text{-}I} > 5,5'\text{-}H >$$
$$\underset{(-)}{5,5'\text{-}OH} > \underset{(-)}{5,5'\text{-}Br} > \underset{(-)}{5,5'\text{-}NO_2} > \underset{(-)}{5,5'\text{-}Cl}$$

where (+) indicates electron releasing and (−) electron attracting inductive effects[7].

Experimental

5-Iodosalicylaldehyde was obtained as its sodium salt by the reaction of *p*-iodophenol (10 g.) with chloroform (9 g.) in aqueous sodium hydroxide[8] (9.1 g. sodium hydroxide in 40 ml. water) at 55~65°C. Yield, 14%.

5, 5'-Dihydroxysalicylaldehyde - ethylenediimine.—To a solution of 5-methoxysalicylaldehyde (1.6 g. in 41 ml. ethanol) was added ethylenediamine-monohydrate (520 mg. in 5 ml. ethanol). In the meantime a yellow precipitate separated, which was filtered and dried (1.5 g.). It was dissolved in ethanol and water was added to it drop by drop until turbidity occurred; the product was left to stand for a while, until yellow needles separated, which were filtered and dried. Yield, 0.9 g.; m. p. 250°C (decomp.). It is easily air-oxidized in an ethanolic solution, when left to stand for one day and the color changes into orange to red.

Anal. Found: C, 60.63; H, 5.77; N, 8.00. Calcd. for $C_{16}H_{16}O_4N_2$-H_2O: C, 60.37; H, 5.70; N, 8.80%.

5,5'-Dimethoxysalicylaldehyde - ethylenediimine.—To a solution of 5-methoxysalicylaldehyde (900 mg. in 20 ml. ethanol) was added ethylenediamine-monohydrate (100 mg. in 3 ml. ethanol). In the meantime the whole mass solidified, which was filtered, washed with a little water and recrystallized from ethanol. Yield, 700 mg.; m. p. 165°C.

Anal. Found: C, 65.95; H, 6.38; N, 8.29. Calcd. for $C_{18}H_{20}O_4N_2$: C, 65.84; H, 6.14; N, 8.53%.

5,5'-Dibromo-, 5,5'-diiodo-, 5,5'-dimethoxysalicylaldehyde-ethylenediimine-copper were obtained by the usual procedure[3,4].

5, 5' - Dibromosalicylaldehyde - ethylenediimine - copper.—Gold orange 5-bromosalicylaldehyde-copper was converted into green 5,5'-dibromosalicylaldehyde-ethylenediimine-copper. Recrystallization of the product from chloroform produced a purple addition compound with chloroform which, upon standing in air, gradually (in two days) lost chloroform to yield the green, pure 5,5'-dibromo-complex.

Anal. Found: C, 39.99; H, 2.86; N, 5.91; Cu, 13.04. Calcd. for $C_{16}H_{12}O_2N_2Br_2Cu$: C, 39.42; H, 2.48; N, 5.75; Cu, 12.97%.

5, 5' - Diiodosalicylaldehyde - ethylenediimine - copper.—Gold yellow 5-iodosalicylaldehyde-copper suspended in boiling ethanol was treated with ethylenediamine-monohydrate; immediately transient green coloration was observed, but the color turned purple and the purple addition compound of 5,5' - diiodosalicylaldehyde - ethylenediimine-copper with ethanol precipitated, which was filtered and recrystallized from ethanol. By heating the addition compound at 110°C for thirty minutes, dark green pure 5,5'-diiodosalicylaldehyde-ethylenediimine-copper was obtained.

6) H. Decker and O. Koch, *Ber.*, **40**, 4794 (1907).
7) C. K. Ingold, *Ann. Repts.*, **23**, 129 (1926).
8) Cf. also H. H. Hodgson and T. A. Jenkinson, *J. Chem. Soc.*, **1927**, 1740; ibid., **1929**, 469.

Anal. Found: C, 33.25; H, 2.42; N, 4.17; Cu, 10.40. Calcd. for $C_{16}H_{12}O_2N_2I_2Cu$: C, 33.04; H, 2.08; N, 4.82; Cu, 10.93%.

5, 5'-Dimethoxysalicylaldehyde - ethylenediimine-copper.—(a) It is obtained from yellow 5-methoxysalicylaldehyde-copper as described above. Recrystallization from chloroform gave green plates. $\lambda_{max}^{C_5H_5N}$ 400, 585 mμ[9].

Anal. Found: C, 53.74; H, 4.59; N, 6.77; Cu, 16.91. Calcd. for $C_{18}H_{18}O_4N_2Cu$: C, 54.45; H, 4.65; N, 7.19; Cu, 16.30%.

(b) 5,5' - Dimethoxysalicylaldehyde - ethylene - diimine (600 mg.) in boiling ethanol (80 ml.) was treated with a saturated aqueous solution containing copper acetate (400 mg.) and the mixture was boiled for thirty minutes on a water bath. After cooling, the precipitates were filtered and recrystallized from chloroform.

(c) To an intimate mixture of 5,5'-dihydroxysalicylaldehyde-ethylenediimine-copper (400 mg.) and dimethylsulfate (400 mg.) was added 0.8 ml. of 10% aqueous sodium hydroxide solution; it reacted exothermically at once, stirred thoroughly to complete the reaction. After an hour, the paste was filtered, washed with water, dried and recrystallized from chloroform.

5, 5'-Dihydroxysalicylaldehyde-ethylenediimine-copper.—To a boiling solution of 5,5'-dihydroxysalicylaldehyde-ethylenediimine (1.2 g. in 215 ml. ethanol) was added copper acetate (0.96 g. in 20 ml. water) and the mixture heated for twenty minutes on a water bath. After the mixture was cooled, the precipitate was filtered and recrystallized from ethanol. It showed blue purple as needles but a gray green color appeared when powdered. Yield, 1 g.

Anal. Found: C, 50.15; H, 4.47; N, 6.64; Cu, 17.27. Calcd. for $C_{16}H_{14}N_2O_4Cu$-H_2O: C, 50.61; H, 4.25; N, 7.38; Cu, 16.74%.

Addition Compound with Propionic Acid[3].—*5, 5'-Diiodosalicylaldehyde-ethylenediimine-copper.*

Anal. Found: C, 33.49; H, 2.70; N, 4.53. Calcd. for $C_{16}H_{12}O_2N_2I_2Cu$-$C_3H_6O_2$: C, 34.79; H, 2.77; N, 4.27%.

5, 5' - Dimethoxysalicylaldehyde - ethylenediimine - copper.

Anal. Found: C, 54.20; H, 5.39; N, 6.10. Calcd. for $C_{18}H_{18}O_4N_2Cu$-$C_3H_6O_2$: C, 54.35; H, 5.21; N, 6.04%.

Addition Compounds with Phenol[3].—*5, 5'-Diiodosalicylaldehyde-ethylenediimine-copper.*

Anal. Found: C, 40.16; H, 2.92; N, 4.18. Calcd. for $C_{16}H_{12}O_2N_2I_2Cu$-C_6H_6O: C, 39.09; H, 2.68; N, 4.15%.

5, 5' - Dimethoxysalicylaldehyde - ethylenediimine - copper.

Anal. Found: C, 58.48; H, 4.85; N, 5.63. Calcd. for $C_{18}H_{18}O_4N_2Cu$-C_6H_6O: C, 59.54; H, 5.00; N, 5.79%.

5, 5' - Dibromosalicylaldehyde-ethylenediimine - copper.—The reaction product was purified by washing with benzene or by recrystallization from chloroform containing phenol.

Anal. Found: C, 43.89, H, 2.92; N, 4.74. Calcd. for $C_{16}H_{12}O_2N_2Br_2Cu$-C_6H_6O: C, 45.41; H, 3.12; N, 4.82%.

5, 5' - Dihydroxysalicylaldehyde - ethylenediimine - copper.—The reaction product was purified by washing repeatedly with benzene, and was not recrystallized.

Anal. Found: C, 55.98; H, 4.89; N, 5.00. Calcd. for $C_{16}H_{14}O_4N_2Cu$-C_6H_6O: C, 57.95; H, 4.42; N, 6.15%.

Addition Compounds with Chloroform.—*5, 5'-Dibromosalicylaldehyde-ethylenediimine-copper.*

Anal. Found: C, 36.23, 36.06; H, 2.48, 2.42; N, 5.56, 5.61. Calcd. for $C_{16}H_{12}O_2N_2Br_2Cu$-$\frac{1}{2}CHCl_3$: C, 36.21; H, 2.30; N, 5.12%. Weight decrease at 110°C. Found: 11.13. Calcd. for $C_{16}H_{12}O_2N_2Br_2Cu$-$\frac{1}{2}CHCl_3$: 10.91%.

5, 5'-Diiodosalicylaldehyde-ethylenediimine - copper.—Recrystallized from chloroform.

Anal. Found: C, 28.54; H, 3.35; N, 4.42. Calcd. for $C_{16}H_{12}O_2N_2I_2Cu$-$CHCl_3$: C, 29.13; H, 3.35; N, 4.00%.

Addition Compound with Ethanol.—*5, 5'-Diiodosalicylaldehyde-ethylenediimine-copper.*

Anal. Found: C, 32.43; H, 2.88; N, 4.62. Calcd. for $C_{16}H_{12}O_2N_2I_2Cu$-C_2H_6O: C, 34.44; H, 2.89; N, 4.46%. Weight decrease at 110°C. Found: 6.34. Calcd. for $C_{16}H_{12}O_2N_2I_2Cu$-C_2H_6O: 7.34%.

The author is grateful to Mr. M. Shito and Miss S. Indo for the microanalysis.

Faculty of Liberal Arts
Saga University
Honjo, Saga

9) Beckman E. P. U. spectrophotometer.