Metal Complexes with Terdentate Ligands. II[1]. *Synthesis and Properties of Tri-coordinated Copper(II) Complexes*[2]

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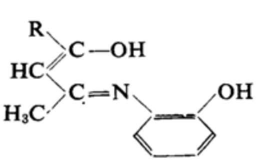
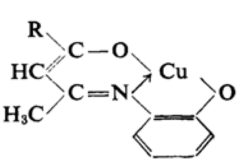
(Received February 13, 1960)

So-called tri-coordinated copper(II) complexes have been reported by several investigators. For instance, Pfeiffer et al.[3] have prepared salicylaldehyde-2-hydroxyanil copper(II), while Yamaguchi[4], Dikmen et al.[5] and the present author[6] have synthesized salicylaldehyde-2-hydroxybenzylimine copper(II). Although it is presumed that the copper atoms in these chelates have an unusual coordination number, three, it is desirable to study extensively tri-coordinated copper(II) complexes having different types of ligand molecules in order to obtain more definite information about the tri-coordination of the copper atoms. This paper presents the synthesis and properties of some tri-coordinated copper(II) complexes.

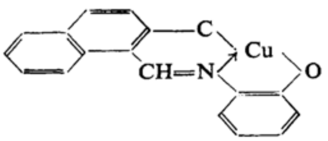
I. Copper(II) Complexes having Schiff Bases of 2-Aminophenol.—In order to obtain terdentate ligands of similar type to salicylaldehyde-2-hydroxyanil, the present author prepared acetylacetone-mono-(2-hydroxyanil) and benzoylacetone-mono-(2-hydroxyanil) by the condensation of 2-aminophenol with acetylacetone and benzoylacetone, respectively. It is expected that they act as terdentate ligands in their enol forms shown in A′ and B′. That is to say, they have two hydrogen atoms capable of being replaced by metal atoms (i. e., hydrogen



A′ R: CH_3
B′ R: C_6H_5*



A R: CH_3
B R: C_6H_5



C

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1) Y. Muto, This Bulletin, 31, 1017 (1958).

2) This was presented partly in a previous paper (Y. Muto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 76, 1405 (1955).), and partly at the Symposium on Co-ordination Compounds held by the Chemical Society of Japan in Fukuoka on October 21, 1959.

3) P. Pfeiffer, Th. Hesse, G. Pfizner, W. Scholl and H. Thielert, *J. prakt. Chem.*, **149**, 217 (1937).

4) M. Yamaguchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 261 (1954).

5) C. Dikmen and T. Günduz, *Ber.*, **89**, 2637 (1956).

6) Y. Muto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 274 (1953).

* It is known that primary amines condense with benzoylacetone to form Schiff bases having a general formula $C_6H_5CO\cdot CH_2C(=N-R)\cdot CH_3$. Therefore, benzoylacetone-mono-(2-hydroxyanil) must have the structure shown in B′, althogh it may be presumed that the anil has the structure, $C_6H_5C(=N-C_6H_4OH)\cdot CH_2CO\cdot CH_3$.

of the phenolic and enolic hydroxyl groups) as well as a nitrogen atom capable of being coordinated to a metal atom (i. e., nitrogen of an azomethine group). Therefore, they will react with copper(II) ion to form chelates having a five-membered ring and a six-membered one, which are very common. On being treated with copper(II) acetate, they yielded complexes having the compositions expected for the formulae A and B. Similarly, 2-hydroxynaphthaldehyde-(1)-[*o*-hydroxyanil] yielded a copper(II) complex having the composition shown in C.

These complexes were readily soluble in pyridine, slightly soluble in nitrobenzene, and soluble with difficulty in other common organic solvents. When these complexes were recrystallized from pyridine, the corresponding monopyridinates were formed. The pyridinates liberated pyridine gradually at 70°C and completely at 120°C. The decrease in weight corresponded to one molecule of pyridine per one atom of copper. From these facts, it seems very likely that these pyridine-free complexes have two interlocked chelate rings shown in A, B and C, although their structures might not be so simple as is implied by the ordinary chemical formulae. This conclusion has been suggested further by magnetochemical studies[7,8]. As the present author et al. have already reported in previous papers[7,8], these pyridine-free complexes show magnetic moments considerably smaller than the theoretical value predicted from the presence of one odd electron, and the subnormal moments suggest the presence of dimeric molecules, in which two copper atoms are very close to each other as in copper(II) acetate monohydrate crystals, whereas the pyridinates have the normal moments expected for tetra-coordinated copper(II) complexes (Table I).

It has been presumed by the method of ligand-exchange[9] that these tri-coordinated complexes are more stable than the tetra-coordinated complexes having ligands similar to A′ or B′ from the structural point of view, but that they are less stable than bis-8-oxyquinolin copper(II) or salicylaldehyde-ethylenediimine copper(II) (Table II). For instance, when an alcoholic solution of benzoylacetone-mono-(2-hydroxyanil) was mixed with an alcoholic solution of bis-salicylaldehydeanil copper(II), benzoylacetone-mono-(2-hydroxyanil) copper(II) was formed, whereas the reverse reaction of this exchange did not take place.

II. Copper(II) Complexes Having Schiff Bases of Anthranilic Acid. — These complexes were synthesized by essentially the same method as that described in I. Namely, anthranilic acid was subjected to condensation with 5-*X*-salicylaldehyde (*X*-: chloro-, bromo- or nitro-), and the resulting Schiff bases (Formula D′) were treated with copper(II) acetate. In this

TABLE I. THE MAGNETIC MOMENTS OF TRI-COORDINATED COPPER(II) COMPLEXES AND THEIR PYRIDINATES

Chelates	μ (B. M.)	Reference
Salicylaldehyde-2-hydroxybenzylimine Cu(II)	0.87	7
Monopyridino-salicylaldehyde-2-hydroxybenzylimine Cu(II)	1.83	7
Salicylaldehyde-2-hydroxyanil Cu(II)	1.34	7
Monopyridino-salicylaldehyde-2-hydroxyanil Cu(II)	1.84	7
Acetylacetone-mono-(2-hydroxyanil) Cu(II)	1.37	7
Monopyridino-acetylacetone-mono-(2-hydroxyanil) Cu(II)	1.81	7
Benzoylacetone-mono-(2-hydroxyanil) Cu(II)	1.11	7
Monopyridino-benzoylacetone-mono-(2-hydroxyanil) Cu(II)	1.84	7
2-Hydroxynaphthaldehyde-(1)-[*o*-hydroxyanil] Cu(II)	1.39	8
Monopyridino-2-hydroxynaphthaldehyde-(1)-[*o*-hydroxyanil] Cu(II)	1.77	8
5-Bromosalicylalanthranilic acid Cu(II)	1.87	8
Monopyridino-5-bromosalicylalanthranilic acid Cu(II)	1.86	8
5-Nitrosalicylalanthranilic acid Cu(II)	1.87	8
Monopyridino-5-nitrosalicylalanthranilic acid Cu(II)	1.84	8
Salicylaldehyde-2-mercaptoanil Cu(II)	1.82*	
2-Hydroxy-5-methylbenzaldehyde-*o*-mercaptoanil Cu(II)	1.93*	
5-Bromosalicylaldehyde-*o*-mercaptoanil Cu(II)	1.76*	

* The magnetic susceptibilities were determined by the Gouy method at room temperature (28~31°C).

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[7] M. Kishita, Y. Muto and M. Kubo, *Naturwissenschaften*, **44**, 372 (1957); *Australian J. Chem.*, **10**, 386 (1957).

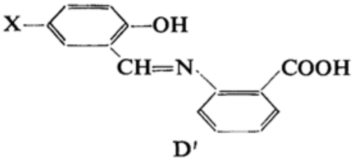
[8] M. Kishita, Y. Muto and M. Kubo, *Naturwissenschaften*, **44**, 612 (1957); *Australian J. Chem.*, **11**, 309 (1958).

[9] Y. Muto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 252 (1955).

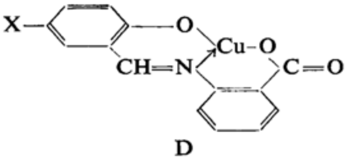
TABLE II. THE LIGAND-EXCHANGE REACTIONS

Chelates	Replacing agents	Resulting chelates	Analysis Cu % Calcd.	Analysis Cu % Found	Analysis N % Calcd.	Analysis N % Found
Bis-acetylacetone Cu(II)	Acetylacetone-mono-(2-hydroxyanil)	Acetylacetone-mono-(2-hydroxyanil) Cu(II)	25.14	25.08	5.54	5.71
Bis-benzoylacetone Cu(II)	Benzoylacetone-mono-(2-hydroxyanil)	Benzoylacetone-mono-(2-hydroxyanil) Cu(II)	20.18	20.15	4.45	4.49
Bis-2-hydroxynaphthaldehyde-(1) Cu(II)	2-Hydroxynaphthaldehyde-(1)-[*o*-hydroxyanil]	2-Hydroxynaphthaldehyde-(1)-[*o*-hydroxyanil] Cu(II)	19.52	19.38	4.40	4.54
Bis-salicylaldimine Cu(II)	Benzoylacetone-mono-(2-hydroxyanil)	Benzoylacetone-mono-(2-hydroxyanil) Cu(II)	20.18	20.09	4.45	4.54
Bis-salicylaldehyde-anil Cu(II)	Acetylacetone-mono-(2-hydroxyanil)	Acetylacetone-mono-(2-hydroxyanil) Cu(II)	25.14	25.16	5.54	5.64
Bis-dimethylglyoxime Cu(II)	Benzoylacetone-mono-(2-hydroxyanil)	Benzoylacetone-mono-(2-hydroxyanil) Cu(II)	20.18	20.23	4.45	4.57
Bis-ethylacetoacetate Cu(II)	Acetylacetone-mono-(2-hydroxyanil)	Acetylacetone-mono-(2-hydroxyanil) Cu(II)	25.14	25.13	5.54	5.67
Benzoylacetone-mono-(2-hydroxyanil) Cu(II)	8-Oxyquinoline	Bis-8-oxyquinoline Cu(II)	18.06	18.11	7.96	8.02
Acetylacetone-mono-(2-hydroxyanil) Cu(II)	Salicylaldehyde-ethylene-diimine	Salicylaldehyde-ethylene-diimine Cu(II)	19.27	19.20	8.49	8.61

way the complexes having the compositions shown in D were obtained. These complexes were soluble with difficulty in common organic solvents such as ethanol or benzene, while their monopyridinates were soluble in ethanol to a certain extent. Pyridine could be removed from the pyridinates by heating at about 150~200°C in air or boiling in ethanol.



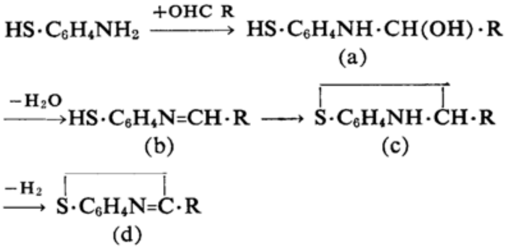
D′



D

X: Cl, Br, NO_2

III. Copper(II) Complexes Having Schiff Bases of 2-Aminothiophenol.—Unlike the case of 2-aminophenol or anthranilic acid, 2-aminothiophenol condenses with aldehydes to form benzothiazoles. It seems probable from the results of several investigators[10] that the mechanism of the reaction can be represented as follows:



$$HS\cdot C_6H_4NH_2 \xrightarrow{+OHC\ R} HS\cdot C_6H_4NH\cdot CH(OH)\cdot R \quad (a)$$

$$\xrightarrow{-H_2O} HS\cdot C_6H_4N{=}CH\cdot R \ (b) \longrightarrow S\cdot C_6H_4NH\cdot CH\cdot R \ (c)$$

$$\xrightarrow{-H_2} S\cdot C_6H_4N{=}C\cdot R \ (d)$$

Although the thiazolines (c) were isolated as intermediates in the formation of the thiazoles (d) from 2-aminothiophenol and aldehydes, neither the aldols (a) nor the anils (b) have been isolated.

Claasz[10] obtained 2-(*o*-hydroxyphenyl)benzothiazol (m.p. 130°C) by the reaction of 2-aminothiophenol with salicylaldehyde. Recently, Charles and Freiser[11] have obtained 2-(*o*-hydroxyphenyl)benzothiazoline (m.p. 136~137°C). However, in the course of this study, the present author has mixed 2-aminothiophenol and salicylaldehyde in ethanol and obtained a product of m.p. 148~148.5°C. This compound was converted into 2-(*o*-hydroxyphenyl)benzothiazol when it was recrystallized from ethanol containing a small amount of hydrogen chloride. On oxidation with hydrogen peroxide, this compound yielded 2-salicylaminophenyldisulfide, $(HO\cdot C_6H_4CH{=}N\cdot C_6H_4S-)_2$, indicating the presence of a mercapto group. The elementary analysis of this compound agreed with the formula $HO\cdot C_6H_4CH{=}N\cdot C_6H_4SH$. On treating this compound with

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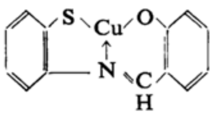
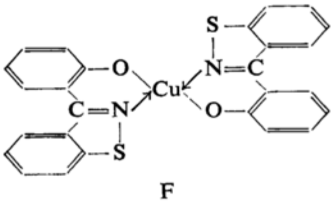
[10] M. Claasz, *Ber.*, **45**, 1031 (1912); **49**, 1141 (1916); M. T. Bogert and A. Stull, *J. Am. Chem. Soc.*, **47**, 3038 (1925); H. P. Lankelma and P. X. Sharnoff, ibid., **53**, 2654 (1931); M. T. Bogert and B. Naiman, ibid., **57**, 1529 (1935).

[11] R. G. Charles and H. Freiser, *J. Org. Chem.*, **18**, 422 (1953).

copper(II) acetate, it yielded a complex having a composition agreeing with the formula E.



E



F

This complex was also prepared by the condensation of bis-salicylaldehyde copper(II) with 2-aminothiophenol. This formula was suggested further by the following observations. First, when this complex was decomposed by dilute sulfuric acid, salicylaldehyde was liberated. If this complex had had a thiazol or thiazoline link, salicylaldehyde would not have been liberated from it. Secondly, when this complex was recrystallized from pyridine, its monopyridinate was formed in the same manner as the tri-coordinated copper(II) complexes described in I and II. This shows that the composition of the complex has the molar ratio 1 : 1 of copper(II) to the ligand molecule.

As an example of metal complexes having the Schiff base of 2-aminothiophenol, only the following zinc complex has been reported. Bogert and Naiman[10] have shown that zinc 2-aminothiophenolate could be condensed directly with aromatic aldehydes to form zinc complexes having a general formula $(R\cdot CH{=}N\cdot C_6H_4S-)_2Zn$, which yielded 2-R-benzothiazoles when they were boiled in glacial acetic acid. The present author has also found that the corresponding 2-R-benzothiazoline does not form zinc or copper(II) complexes, while 2-(*o*-hydroxyphenyl)benzothiazol forms a copper(II) complex having the molar ratio 1 : 2 of copper(II) to the ligand molecule as shown in F. This result suggests that the thiazolines (c) cannot be converted into anils (b) by the action of metal ions. Therefore, the fact that reaction product of 2-aminothiophenol with salicylaldehyde (m. p. 148~148.5°C) yielded a complex having the composition shown in E gives support to the conclusion that the product must be salicylaldehyde-2-mercaptoanil.

2-Hydroxy-5-methylbenzaldehyde-*o*-mercaptoanil copper(II), 5-bromosalicylaldehyde-*o*-mercaptoanil copper(II) and their monopyridinates could be prepared in an analogous way.

Experimental

Preparation of Copper(II) Complexes.—Appropriate amines were subjected to condensation with suitable ketones or aldehydes in ethanol. The resulting Schiff bases were separated and were treated with copper(II) acetate in the mixture of ethanol and water. The crude products which precipitated were separated, dissolved in pyridine and filtered. When water was added to the filtrates, the monopyridinates of the complexes were formed as crystals. On heating to an appropriate temperature (100~200°C), almost all the pyridine was removed. To ensure the complete removal, the residue were boiled in ethanol on a water bath for about half an hour. After being allowed to cool, the precipitates were filtered and dried at about 90°C. In this way pyridine-free copper(II) complexes were prepared. None of them melted below 300°C.

(1) **Acetylacetone-mono-(2-hydroxyanil) Copper(II).**—This was prepared from copper(II) acetate and acetylacetone-mono-(2-hydroxyanil)[12] (m. p. 187°C, yellow prismatic crystals. Found: N, 7.48. Calcd. for $C_{11}H_{13}O_2N$: N, 7.33%). The copper(II) chelate formed green prismatic crystals, while its pyridinate crystallized as deep green plates.

Found: N, 5.78; Cu, 25.32. Calcd. for $C_{11}H_{11}\cdot O_2NCu$: N, 5.54; Cu, 25.14%. Found: N, 8.69; Cu, 19.34; py., 23.73. Calcd. for $C_{11}H_{11}O_2NCu\cdot C_5H_5N$, N, 8.44; Cu, 19.15; py., 23.84%.

(2) **Benzoylacetone-mono-(2-hydroxyanil) Copper(II).**—Benzoylacetone-mono-(2-hydroxyanil) was prepared by the condensation of benzoylacetone (1.7 g.) with 2-aminophenol (1.1 g.) in ethanol (30 ml.). It was isolated in the form of yellow prismatic crystals; m. p. 169~170°C, yield 2 g.

Found: C, 75.76; H, 6.02; N, 5.81. Calcd. for $C_{16}H_{15}O_2N$: C, 75.87; H, 5.97; N, 5.53%.

The copper(II) chelate formed yellow-green needles, while its pyridinate crystallized as deep green plates.

Found: N, 4.49; Cu, 20.19. Calcd. for $C_{16}H_{13}\cdot O_2NCu$: N, 4.45; Cu, 20.18%. Found: N, 7.01; Cu, 16.23; py., 19.69. Calcd. for $C_{16}H_{13}O_2NCu\cdot C_5H_5N$: N, 7.09; Cu, 16.09; py., 20.03%.

(3) **2-Hydroxynaphthaldehyde-(1)-[*o*-hydroxyanil] Copper(II).**—This was prepared from copper(II) acetate and 2-hydroxynaphthaldehyde-(1)-[*o*-hydroxyanil][13] (m.p. 248~249°C, brown-red needles, Found: N, 5.41. Calcd. for $C_{17}H_{13}O_2N$: N, 5.32%). The copper(II) chelate was yellow-green, while its pyridinate was brown. Both crystallized as needles.

Found: N, 4.40; Cu, 19.52. Calcd. for $C_{17}H_{11}\cdot O_2NCu$: N, 4.31; Cu, 19.56%. Found: N, 6.99; Cu, 15.71; py., 19.39. Calcd. for $C_{17}H_{11}O_2NCu\cdot C_5H_5N$: N, 6.94; Cu, 15.73; py., 19.59%.

(4) **5-Chlorosalicylalanthranilic Acid Copper(II).**—5-Chlorosalicylalanthranilic acid was prepared by the condensation of 5-chlorosalicylaldehyde (1.6 g.) with anthranilic acid (1.4 g.) in ethanol (50 ml.). It was isolated in the form of orange prismatic crystals; m. p. 200°C, yield 2 g.

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[12] W. Suida, *J. prakt. Chem.*, [2] **83**, 241 (1911).

[13] A. Senier and R. Clarke, *J. Chem. Soc.*, **99**, 2082 (1911—2).

Found: C, 61.10; H, 3.63; N, 5.39. Calcd. for $C_{14}H_{10}O_3NCl$: C, 60.99; H, 3.66; N, 5.08%.

The copper(II) chelate formed greenish brown needles, while its pyridinate crystallized as bright green plates.

Found: N, 4.29; Cu, 18.63. Calcd. for $C_{14}H_8 \cdot O_3NClCu$: N, 4.15; Cu, 18.84%. Found: N, 6.83; Cu, 14.98; py., 19.24. Calcd. for $C_{14}H_8O_3NClCu \cdot C_5H_5N$: N, 6.73; Cu, 15.26; py., 19.00%.

(5) **5-Bromosalicylalanthranilic Acid Copper(II).**—5-Bromosalicylalanthranilic acid was prepared by the condensation of 5-bromosalicylaldehyde (2 g.) with anthranilic acid (1.5 g.) in ethanol (50 ml.). It was isolated in the form of orange prismatic crystals; m. p. 202°C, yield 3 g.

Found: C, 52.47; H, 3.12; N, 4.48. Calcd. for $C_{14}H_{10}O_3NBr$: C, 52.52; H, 3.15; N, 4.38%.

The copper(II) chelate formed greenish brown needles, while its pyridinate crystallized as bright green plates.

Found: N, 3.96; Cu, 16.87. Calcd. for $C_{14}H_8 \cdot O_3NBrCu$: N, 3.71; Cu, 16.82%. Found: N, 6.30; Cu, 13.86; py., 17.36. Calcd. for $C_{14}H_8O_3NBrCu \cdot C_5H_5N$; N, 6.08; Cu, 13.79; py., 17.17%.

(6) **5-Nitrosalicylalanthranilic Acid Copper(II).**—5-Nitrosalicylalanthranilic acid was prepared by the condensation of 5-nitrosalicylaldehyde (1.7 g.) with anthranilic acid (1.4 g.) in ethanol (50 ml.). It was isolated in the form of red prismatic crystals; m. p. 271°C, yield 2.2 g.

Found: C, 58.67; H, 3.48; N, 10.04. Calcd. for $C_{14}H_{10}O_5N_2$: C, 58.74; H, 3.52; N, 9.79%.

The copper(II) chelate was greenish brown, while its pyridinate was bright green. Both formed prismatic crystals.

Found: N, 7.80; Cu, 18.43. Calcd. for $C_{14}H_8 \cdot O_5N_2Cu$: N, 8.06; Cu, 18.27%. Found: N, 10.12; Cu, 15.15; py., 18.31. Calcd. for $C_{14}H_8O_5N_2Cu \cdot C_5H_5N$: N, 9.85; Cu, 14.89; py., 18.53%.

(7) **Salicylaldehyde-2-mercaptoanil Copper(II).**—*a*) *Salicylaldehyde-2-mercaptoanil.*—Equimolar amounts (0.01 mol.) of 2-aminothiophenol and salicylaldehyde were dissolved in ethanol (30 ml.). The resulting solution was kept below 30°C by means of a cold water bath for about two hours; meanwhile the crude product precipitated. Recrystallization from ether gave colorless prismatic crystals; m. p. 148∼148.5°C, yield 1.5 g.

Found: C, 68.27; H, 5.11; N, 6.08. Calcd. for $C_{13}H_{11}NOS$: C, 68.10; H, 4.84; N, 6.11%.

b) The copper(II) chelate was prepared by the reaction of salicylaldehyde-2-mercaptoanil described above with copper(II) acetate. This chelate was also obtained by the condensation of bis-salicylaldehyde copper(II) with 2-aminothiophenol in the same way as that described in (9). The pyridine-free complex was deep green, while the pyridinate was brown. Both crystallized as needles.

Found: C, 53.74; H, 3.41; N, 4.67; Cu, 21.80. Calcd. for $C_{13}H_9NOSCu$: C, 53.69; H, 3.12; N, 4.82; Cu, 21.85%. Found: N, 7.70; Cu, 17.31; py., 21.39. Calcd. for $C_{13}H_9NOSCu \cdot C_5H_5N$: N, 7.57; Cu, 17.18; py., 21.38%.

c) *Oxidation of Salicylaldehyde-2-mercaptoanil.*—Salicylaldehyde-2-mercaptoanil (0.5 g.) was dissolved in a mixture of ethanol (20 ml.) and aqueous hydrogen peroxide (30%, 5 ml.). After being heated gently on a water bath for ten minutes, the solution was allowed to stand overnight in air at room temperature; meanwhile yellow crystals precipitated. Recrystallization from benzene gave yellow needles; m. p. 171°C, yield 0.3 g. When this product was mixed with 2-salicylaminophenyldisulfide, the melting point was unaltered.

Found: N, 6.26. Calcd. for $C_{26}H_{16}O_2N_2S_2$: N, 6.19%.

(8) **5-Bromosalicylaldehyde-*o*-mercaptoanil Copper(II).**—5-Bromosalicylaldehyde-*o*-mercaptoanil was prepared by the condensation of 5-bromosalicylaldehyde (2 g.) with 2-aminothiophenol (1.3 g.) in the same way as that described in (7). It was isolated in the form of colorless prismatic crystals; m. p. 147°C, yield 2 g.

Found: C, 50.90; H, 3.60; N, 4.31. Calcd. for $C_{13}H_{10}NOSBr$: C, 50.66; H, 3.27; N, 4.54%.

The copper(II) chelate was deep green, while its pyridinate was brown-red. Both crystallized as needles.

Found: C, 41.89; H, 2.42; N, 3.84; Cu, 17.25. Calcd. for $C_{13}H_8NOSBrCu$: C, 42.23; H, 2.18; N, 3.79; Cu, 17.19%. Found: N, 6.42; Cu, 14.30; py., 17.66. Calcd. for $C_{13}H_8NOSBrCu \cdot C_5H_5N$: N, 6.24; Cu, 14.16; py., 17.62%.

(9) **2-Hydroxy-5-methylbenzaldehyde-*o*-mercaptoanil Copper(II).**—A solution of 2-aminothiophenol (0.7 g.) in ethanol (10 ml.) was added to a boiling solution of bis-2-hydroxy-5-methylbenzaldehyde copper(II) (1.7 g.) in ethanol (50 ml.). Deep green micro-crystals immediately precipitated. It was purified by recrystallization from pyridine. The copper(II) chelate was deep green, while its pyridinate was brown-red. Both crystallized as needles.

Found: C, 55.10; H, 3.87; N, 4.47; Cu, 20.85. Calcd. for $C_{14}H_{11}NOSCu$: C, 55.16; H, 3.64; N, 4.59; Cu, 20.84%. Found: N, 7.45; Cu, 16.59; py., 20.63. Calcd. for $C_{14}H_{11}NOSCu \cdot C_5H_5N$: N, 7.30; Cu, 16.55; py., 20.60%.

(10) **Bis-2-(*o*-hydroxyphenyl)benzothiazol Copper(II).**—A solution of copper(II) acetate monohydrate (0.5 g.) in water (30 ml.) was added to a boiling solution of 2-(*o*-hydroxyphenyl)benzothiazol (0.6 g.) in ethanol (30 ml.). Dark green micro-crystals immediately precipitated. Recrystallization from pyridine gave dark green plates. Yield 0.7 g.

Found: N, 5.40; Cu, 12.38. Calcd. for $C_{26}H_{16} \cdot O_2N_2S_2Cu$: N, 5.31; Cu, 12.31%.

Bis-2-(*o*-hydroxy-*m*-bromophenyl)benzothiazol copper(II) could be prepared in a similar manner. It was isolated in the form of dark green plates.

Found: N, 4.21; Cu, 9.52. Calcd. for $C_{26}H_{14} \cdot O_2N_2S_2Br_2Cu$: N, 4.16; Cu, 9.43%.

Decomposition of Complexes (7), (8) and (9).—The complexes described in (7), (8) and (9) were decomposed by dilute sulfuric acid and then subjected to steam distillation. Salicylaldehyde, 5-bromosalicylaldehyde and 2-hydroxy-5-methylbenzaldehyde in the distillates were identified by their phenylhydrazones which melted at 143°C, 151°C and 149°C respectively.

Reaction of 2-R-benzothiazolines with Zinc or Copper(II) Acetate.—The reaction of 2-phenylbenzothiazoline with zinc or copper(II) acetate was attempted in organic solvents such as ethanol, pyridine or acetic acid, but the product isolated was only 2-phenylbenzothiazol. Similarly, 5-chloro-2-phenylbenzothiazoline did not form zinc or copper(II) complex.

Exchange Experiments.—Calculated amounts of appropriate reagents and suitable complexes were dissolved or suspended in ethanol. The mixtures were heated on a water bath for about five minutes. The resulting complexes were separated, washed with hot ethanol repeatedly and then dried at 80°C. The elementary analysis of the resulting complexes is presented in Table II.

The author is grateful to Mr. Michihiko Kishita of Nagoya University for measurements of magnetic susceptibilities and to Mr. Michio Shido of Kyushu University for elementary analyses.

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