Redistillation gave 51 g. (67% yield) of 2,2-dimethyl-1-oxa-2-silacyclohexane, b.p. 122–125°, n^{25}D 1.4260.

Anal. Calcd. for $C_6H_{14}OSi$: C, 55.38; H, 10.77; Si, 21.54; mol. wt., 130. Found: C, 55.61; H, 10.83; Si, 21.30; mol. wt., 133.

5-Chloropentoxydimethylchlorosilane (Id).—Tetrahydropyran (42 g., 0.49 mole) and dimethyldichlorosilane (129 g., 1.0 mole) were mixed and heated at 200° for 4 hours under autogenous pressure. Distillation gave 53.5 g. (51% yield) of 5-chloropentoxydimethylchlorosilane, b.p. 57° (0.6 mm.).

Anal. Calcd. for $C_7H_{16}Cl_2OSi$: C, 39.07; H, 7.45; Cl, 33.02. Found: C, 39.36; H, 7.57; Cl, 32.88.

An attempt to combine tetrahydropyran and dimethyldichlorosilane at reflux temperature in the presence of anhydrous zinc chloride was unsuccessful.

2,2-Dimethyl-1-oxa-2-silacycloheptane (IId).—5-Chloropentoxydimethylchlorosilane (50.3 g., 0.23 mole) was added slowly to a stirred mixture of lithium (3.25 g., 0.47 mole) in 300 ml. of refluxing decane. Refluxing and stirring were continued overnight, resulting in complete disappearance of the lithium. The reaction mixture was filtered and distilled to give 7.1 g. (21% yield) of product, b.p. 143–146°. Analysis of this product after it had been allowed to stand for several days showed it to be a polymer of 2,2-dimethyl-1-oxa-2-silacycloheptane.

Anal. Calcd. for $C_7H_{16}OSi$: C, 58.33; H, 11.11; Si, 19.44; mol. wt., 144. Found: C, 56.81; H, 10.8; Si, 19.18; mol. wt., 537, 524.

A freshly distilled sample has a molecular weight of 248, indicating that the ring-opening polymerization is fairly rapid. Comparison of the boiling point of this material with those of its homologs strongly suggests that it distils as the seven-membered ring compound and not as a dimer.

The 4,4,6,6-Tetramethyl-5-oxa-4,6-disila-1,9-nonanediol (IIIa).—2,2-Dimethyl-1-oxa-2-silacyclopentane (50 g., 0.45 mole) was distilled into a solution of 9 ml. of water and 0.5 ml. of hydrochloric acid in 250 ml. of acetone. This mixture was allowed to stand for four days. Removal of the acetone and distillation of the residue gave 40.6 g. (75% yield) of 4,4,6,6-tetramethyl-5-oxa-4,6-disila-1,9-nonanediol, b.p. 75° (20 mm.), n^{26}D 1.4470.

Anal. Calcd. for $C_{10}H_{26}O_3Si_2$: C. 48.00; H, 10.40; Si, 22.40; mol. wt., 250. Found: C, 48.24; H, 10.52; Si, 22.47; mol. wt., 248.

Condensation of Toluene Diisocyanate with 4,4,6,6-Tetramethyl-5-oxa-4,6-disila-1,9-nonanediol.—The diol (2.2 g.) and toluene diisocyanate (1.65 g.) were mixed with three drops of triethylamine. An exothermic reaction took place and the product was heated on a steam-bath for 1.5 hours to give a hard, clear yellow solid which was leached with chloroform. The chloroform solution was filtered and the polymer was precipitated by adding the filtrate to petroleum ether. The polymer became insoluble before its molecular weight could be determined.

Anal. Calcd. for $(C_{19}H_{32}O_5N_2Si_2)_x$: C, 53.78; H, 7.55; Si, 13.28. Found: C, 54.58; H, 7.62; Si, 13.14.

The 4,4,6,6-Tetraphenyl-5-oxa-4,6-disila-1,9-nonanediol (IIIb).—2,2-Diphenyl-1-oxa-2-silacyclopentane (5 g., 0.021 mole) was dissolved in 50 ml. of dioxane. Water was added until the cloud point was reached. Five drops of concentrated hydrochloric acid was added and the solution was clarified by the addition of dioxane. The solution was heated on a steam-bath for 1.5 hours and allowed to stand for two days after which the volatile liquids were removed at 20 mm. pressure. The residue, a light straw-colored, viscous liquid, was heated at 65° for 10 minutes at 0.3 mm. Trituration in petroleum ether caused solidification. Recrystallization from cyclohexane gave 2.2 g. of 4,4,6,6-tetraphenyl-5-oxa-4,6-disila-1,9-nonanediol, m.p. 104–108°. A second recrystallization from cyclohexane raised the melting point to 110–111°. Infrared analysis supported the assigned structure.

Anal. Calcd. for $C_{30}H_{34}O_3Si_2$: C, 72.29; H, 6.83; mol. wt., 498. Found: C, 72.25; H, 6.77; mol. wt., 485.

5,5,7,7-Tetramethyl-6-oxa-5,7-disila-1,11-undecanediol (IIIc).—2,2-Dimethyl-1-oxa-2-silacyclohexane (30.5 g., 0.23 mole) and water (4.4 ml., 0.25 mole) were mixed and stirred. An exothermic reaction took place which caused a temperature rise to 50°. To ensure completion of the reaction, 10 ml. of acetone, 3 drops of hydrochloric acid and another 1 ml. of water were added. After standing two days, the acetone was removed from the clear, colorless solution at a pressure of 15 mm. To remove the excess water, the crude product was heated to 40° (0.13 mm.). Under these conditions, ebullition occurred and the product slowly vaporized. The vapors were not condensed by cold water but could be trapped at solid carbon dioxide temperature. The distillation was interrupted and the condensed liquid, A, n^{25}D 1.4492, and the distillation residue, B, n^{25}D 1.4495, were analyzed separately. The infrared spectra of A and B were identical and were in agreement with the proposed structure.

Anal. Calcd. for $C_{12}H_{30}O_3Si_2$: C, 51.81; H, 10.79; Si, 20.14; mol. wt., 278. Found for A: C, 51.24; H, 10.90; Si, 20.06; mol. wt., 320. Found for B: C, 51.60; H, 10.87.

WILMINGTON 98, DEL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SAGA UNIVERSITY]

Some Addition Compounds of Bis-salicylaldehyde-ethylenediimine-copper. Part II

BY TSUGUO TANAKA

RECEIVED DECEMBER 30, 1957

The absorption spectra of bis-salicylaldehyde-ethylenediimine-copper in various solvents were measured. The absorption maxima of band II can be correlated with the formation of addition compounds. Three 5,5′-disubstituted bis-salicylaldehyde-ethylenediimine-coppers were prepared, and their formation of addition compounds with propionic acid and phenol was investigated; the methyl substituent facilitates the formation of an addition compound, while the chloro and nitro substituents retard it.

The description of Pfeiffer, *et al.*,[1] of the color of bis-salicylaldehyde-ethylenediimine-copper in various solvents led to the isolation of the addition compounds of the complex with acids and phenols.[2] Attempts were then made to correlate the absorption spectrum in a given solvent with the formation of an addition compound between the complex and the solvent, and to ascertain the nature of the bond between the acid (or phenol) and the complex.

The absorption spectra of bis-salicylaldehyde-ethylenediimine-copper in methyl alcohol and in absolute ethyl alcohol were reported by Tsumaki[3] and Kiss, *et al.*,[4] respectively, but their data do not agree. According to Tsuchida and Tsumaki,[5,3] band I (566 mμ) is due to excitation of the 3 d electron of the copper atom, band II (357 mμ) to the

---

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

[2] T. Tanaka, *Bull. Chem. Soc. Japan*, **29**, 93 (1956).

[3] T. Tsumaki, *ibid.*, **13**, 252 (1938).

[4] A. v. Kiss, P. Csokan and G. Nyiri, *Z. physik. Chem., Abt. A.*, **190**, 65 (1942).

[5] R. Tsuchida, "The Colors and the Structures of the Metal Complexes," Zoshindo, Osaka, 1947, p. 160; T. Tsumaki and R. Tsuchida, *Bull. Chem. Soc. Japan.*, **13**, 527 (1938).

bonds between the ligands and the metal, and band III (270 mμ) to the salicylaldehyde-ethylenediimine moiety.

Kiss reported three bands at 560, 375[6] and 280 mμ. He tried unsuccessfully to explain the absorption spectrum of the metal complex as the sum of the absorption of the chelating agent and that of the metal ion. He observed that, in the absorption spectrum of salicylaldehyde-ethylenediimine in acid medium, band I disappeared and bands II and III shifted to the blue. However, no comparable observation was made of the metal complex.

We have measured the absorption spectra of the complex in various solvents, and our observations are summarized in Table I.

TABLE I

THE ABSORPTION SPECTRA OF BIS-SALICYLALDEHYDE-ETHYLENEDIIMINE-COPPER

Solvents	Absorption maximum in mμ (log ε) Band I	Band II	Band III	
Acetic acid	563(2.22)	345(3.96)		
Propionic acid	560(2.17)	350(3.89)		
p-Cresol	550(2.43)	355(4.13)		
Propionic acid-benzene[a]	559(2.30)	356(4.30)		
Acetic acid–benzene[a]	563(2.39)	357(4.02)		
Phenol–benzene[a]	550(2.38)	358–359(4.19)		
Picric acid[b]	560(2.06)	359(3.86)	270(3.90)	229(4.03)
p-Cresol–benzene[a]	550(2.36)	360(4.43)		
Aniline	564(2.53)	363–365(4.11)		
Anisole	565(2.06)	365–370(3.80)		
Chloroform	564(2.55)	365–370(4.01)		
Benzene	572(2.34)	372(3.68)		
Pyridine	603(2.67)	372(4.27)		

[a] 3 *M* acid or phenol solution in benzene. [b] Alcoholic solution.

The addition compound of the metal complex with a phenol is stable in phenol–benzene solution and gives the characteristic absorption spectrum of the addition compound; however, the addition compounds with acids are comparatively unstable in benzene solution. The effect of the formation of the addition compound on the position of the absorption bands is clearly revealed in band II but not in band I.

Band II.—If the absorption maximum of the complex in benzene (with which the formation of an addition compound need not be considered) is taken as the standard, we find that relatively large shifts toward shorter wave length occur with the acids and with *p*-cresol, compounds which are known to form addition compounds with the complex: 27 mμ for acetic acid, 22 mμ for propionic acid and 17 mμ for *p*-cresol. The absorption maxima for the complex in 3 *M* solutions of the acids or phenols in benzene ranged from 356–360 mμ; these shifts of 12–16 mμ were accompanied by an increase in the extinction coefficient. The addition compound with picric acid, which is stable in alcohol, gave an absorption maximum within this range (359 mμ).

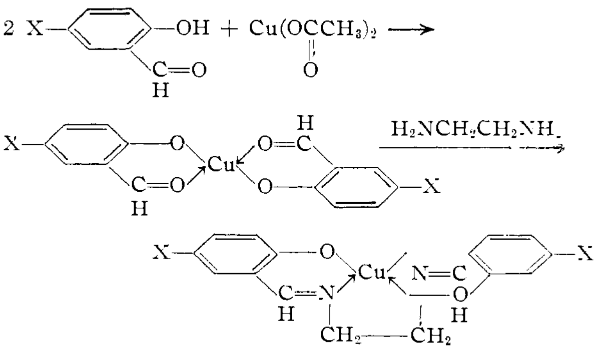
Aniline, anisole and chloroform solutions of the complex showed flat maxima between 363 and 370 mμ (shifts of 2–9 mμ); this may indicate that a weak linkage exists between the solvent and the chelate. No addition compound of the complex with these solvents was isolated; chloroform, however, gave addition compounds with the 5,5′-dinitro and 5,5′-dichloro derivatives of the complex. The observation that no shift occurs in pyridine solution indicates that no addition compound is formed, and none was isolated. Thus band II reveals the formation of an addition compound and the relative stability of this product.

Band I.—In contrast to band II, it is impossible to correlate the absorption maxima of band I with the formation of addition compounds, and the two bands probably have completely different origins.

A large shift to the blue (22 mμ) was observed for the solutions containing phenol or *p*-cresol. The absorption maxima for the complex in acid and acid–benzene solutions and for the picric acid addition compound in alcohol ranged from 559–563 mμ (9–13 mμ shift); those of the aniline, chloroform and anisole solutions from 564–565 mμ. A large shift (31 mμ) toward longer wave length was observed for the complex in pyridine solution, in striking contrast to the absence of any shift in the maximum of band II.

Copper acetate is reported to exist in the aqueous solution as the complex salt rather than the cupric ion,[7] and to crystallize as a dimer.[8] The absorption spectra of the copper acetate crystal has a band at 679 mμ (A band) which shows a strong absorption in the CuO_4 plane, and another band at 375 mμ (B band) which shows a strong absorption in the Cu–Cu direction.[9] The remarkable shifts of the 372 mμ band, observed in the various solvents with which bis-salicylaldehyde-ethylenediimine-copper can form addition compounds, are believed to be due to the conversion from the tetracoördinate planar structure to a pentacoördinate pyramidal structure, as well as to the solvent effect.

The absorption spectra of bis-salicylaldehyde-ethylenediimine-copper in various solvents indicate some of the characteristics of the interaction of bis-salicylaldehyde-ethylenediimine-copper with acids and phenols, but the nature and the mechanism of the reaction were not established. Therefore, some 5,5′-disubstituted bis-salicylaldehyde-ethylenediimine-coppers were synthesized according to the scheme



---

[6] 375 mμ was not recorded, but was found in Fig. 3 and Fig. 7 in the original literature.

(7) J. M. Bolling and J. L. Hall, *West. Va. Univ. Bull., Scr.* **53**, No. 12, 2 (1953); *C. A.*, **48**, 5645a (1954).

(8) J. N. v. Niekerk and F. R. L. Schöning, *Acta Cryst.*, **6**, 227 (1953); R. Tsuchida and S. Yamada, *Nature*, **176**, 1171 (1955).

(9) R. Tsuchida, S. Yamada and H. Nakamura, Symposium on the Metal Complex Salt, 1956, Gakushuin University, Tokyo.

The formation of addition compounds with propionic acid, phenol and chloroform were examined and the results summarized in Table II.

TABLE II

ADDITION COMPOUNDS OF BIS-SALICYLALDEHYDE-ETHYLENEDIIMINE-COPPER DERIVATIVES

Substituents	Color	Addition compound Color (time required for formation, min.) Propionic acid	Phenol	Chloroform
5,5′-CH_3	Bluish-purple	Purple (0.5)	Purple	...
5,5′-H	Green	Purple (30)	Purple	...
5,5′-Cl	Dark green	...	Purple	Blue (20)
5,5′-NO_2	Dark green	...[a]	Brick red	Blue (20, warm)

[a] When bis-5-nitrosalicylaldehyde-ethylenediimine-copper is exposed to the vapor of propionic acid, an unstable purple addition compound is produced; but it decomposes easily and is not obtained in a pure state.

The data in Table II indicate that the tendency of the substituted bis-salicylaldehyde-ethylenediimine-coppers to form the addition compounds decrease in the order

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

where (+) indicates electron-releasing and (−) the electron-attracting inductive effects.[10] The effects of the substituents on the addition of oxygen have been reported.[11]

Experimental

The absorption spectra were measured with a Beckman DU spectrophotometer (cell depth 1.0 cm.). All solvents were purified according to Weissberger.[12]

Bis-5-methylsalicylaldehyde-ethylenediimine-copper.—The following procedure exemplifies the synthesis of the 5,5′-disubstituted bis-salicylaldehyde-ethylenediimine-copper compounds. When a saturated aqueous solution of copper acetate was added gradually to a warm solution of 2 g. of 5-methylsalicylaldehyde in 12 ml. of alcohol, a yellow-green precipitate separated. The reaction mixture was warmed for 10 minutes on a water-bath and then allowed to cool. The precipitate was washed with hot alcohol, dried (yield 2 g. of 5-methylsalicylaldehyde-copper) and dissolved in 36 ml. of alcohol. Ethylenediamine monohydrate (1 g.) was added to the solution. When the green reaction mixture was heated on a water-bath for 20 minutes, it turned purple. The precipitate was washed with hot water and with hot alcohol, and recrystallized from chloroform as blue-purple needles; yield 1.5 g.

Anal. Calcd. for $C_{18}H_{18}N_2O_2Cu$: C, 60.41; H, 5.07; N, 7.83; Cu, 17.75. Found: C, 60.88; H, 5.18; N, 8.23; Cu, 17.30.

Bis-5-chlorosalicylaldehyde-ethylenediimine-copper.—Recrystallization from chloroform gave the blue chloroform addition compound,[13] which upon standing in air lost chloroform to yield the dark green, pure 5-chloro-complex.

Anal. Calcd. for $C_{16}H_{12}N_2O_2Cl_2Cu$: C, 48.21; H, 3.04: N, 7.03; Cu, 15.94. Found: C, 48.03; H, 3.02; N, 7.20; Cu, 16.00.

Bis-5-nitrosalicylaldehyde-ethylenediimine-copper.—This derivative was recrystallized from a large volume of pyridine, as it gives an insoluble addition compound with chloroform; dark green octahedra.

Anal. Calcd. for $C_{16}H_{12}N_4O_6Cu$: C, 45.78; H, 2.88; N, 13.35; Cu, 15.14. Found: C, 46.47; H, 3.51; N, 13.21; Cu, 15.43.

Addition Compounds with Propionic Acid. (a) Bis-salicylaldehyde-ethylenediimine-copper.—When a suspension of this complex in propionic acid was allowed to stand at room temperature, the color changed gradually from green to purple, and in 30 minutes the separation of the addition compound was complete. The addition compound was dried in a vacuum desiccator.

Anal. Calcd. for $C_{19}H_{20}N_2O_4Cu$: C, 56.50; H, 4.99; N, 6.94; Cu, 15.73. Found: C, 56.46; H, 5.04; N, 6.90; Cu, 15.60.

(b) Bis-5-methylsalicylaldehyde-ethylenediimine-copper.

Anal. Calcd. for $C_{21}H_{24}N_2O_4Cu$: C, 58.38; H, 5.60; N, 6.49; Cu, 14.71. Found: C, 58.07; H, 5.37; N, 6.79; Cu, 14.90.

Addition Compounds with Phenol. (a) Bis-5-methylsalicylaldehyde-ethylenediimine-copper.—When a mixture of 100 mg. of this complex and 200 mg. of phenol was fused on a water-bath, an immediate reaction occurred. The mass was washed with benzene and crystallized from chloroform to yield 60 mg. of purple needles.

Anal. Calcd. for $C_{24}H_{24}N_2O_3Cu$: C, 63.78; H, 5.35; N, 6.20; Cu, 14.06. Found: C, 63.00; H, 4.57; N, 6.34; Cu, 13.50.

(b) Bis-5-chlorosalicylaldehyde-ethylenediimine-copper.—The product was not washed with benzene and was recrystallized from chloroform as the recrystallization after washing with benzene yielded only the starting material. The purple addition compound gradually decomposed on exposure to air.

Anal. Calcd. for $C_{22}H_{18}N_2O_3Cl_2Cu$: C, 53.60; H, 3.68; N, 5.69; Cu, 12.89. Found: C, 53.19; H, 3.73; N, 5.93; Cu, 12.70.

(c) Bis-5-nitrosalicylaldehyde-ethylenediimine-copper.—The product which was washed five times with benzene was obtained as brick red cones.

Anal. Calcd. for $C_{22}H_{18}N_4O_7Cu$: C, 51.20; H, 3.52; N, 10.86; Cu, 12.31. Found: C, 50.41; H, 3.26; N, 11.74; Cu, 11.90.

Addition Compounds with Chloroform. (a) Bis-5-chlorosalicylaldehyde-ethylenediimine-copper.—When a suspension of this complex in chloroform was allowed to stand at room temperature for 20 minutes, the blue addition compound was obtained. It decomposed rapidly in air.

Anal. Calcd. for $C_{18}H_{14}N_2O_2Cl_8Cu$: N, 4.40; Cu, 9.97. Found: N, 4.10; Cu, 10.51.

(b) Bis-5-nitrosalicylaldehyde-ethylenediimine-copper.—A blue addition compound was obtained which gradually decomposed in air. The analytical values were not satisfactory.

Acknowledgment.—The author is grateful to Prof. Dr. T. Tsumaki, to Asst. Prof. Dr. K. Kanda and to Mr. H. Ohta (Kyushu University) for their kind advice, to Prof. A. Mizunoe (Saga University) for correcting the English, to Mr. R. Horie, Mr. K. Narikiyo, Mr. T. Nishi, Mr. Y. Matsunaga and Mr. T. Takahashi for their assistance in this work, and to Mr. M. Shito for the microanalyses.

HONJO, SAGA-SHI, JAPAN

---

(10) C. K. Ingold, *Ann. Repts.*, **23**, 129 (1926).

(11) T. Tsumaki, *J. Chem. Soc. Japan*, **58**, 1288 (1937); M. Calvin, R. H. Bailes and W. K. Wilmarth, THIS JOURNAL, **68**, 2254 (1946); M. Calvin and C. H. Barkelew, *ibid.*, **68**, 2257 (1946); W. K. Wilmarth, S. Aranoff and M. Calvin, *ibid.*, **68**, 2263 (1946); M. Calvin and C. H. Barkelew, *ibid.*, **68**, 2267 (1946); E. W. Hughes, W. K. Wilmarth and M. Calvin, *ibid.*, **68**, 2273 (1946).

(12) A. Weissberger and E. S. Proskauer, "Organic Solvents," Interscience Publishers, Inc., New York, N. Y., 1955.

(13) *Cf.* T. Tsumaki and Z. Endo, *J. Chem. Soc. Japan*, **64**, 31 (1943).