The Addition Compounds of Bis-salicylaldehyde Copper(II) and its Derivatives with Pyridine and α, α′-Dipyridyl. II. Some Studies on the Structures

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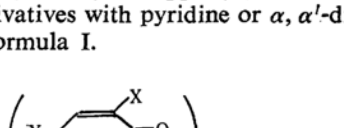
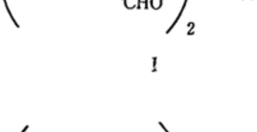
There are studies by several investigators reporting that copper(II) can form a complex with coordination numbers higher than four[1]. In the first paper[2] of this series, the author has reported the isolation of the addition compounds of bis-salicylaldehyde copper(II) and a number of its derivatives with pyridine or α, α′-dipyridyl having Formula I.



I



II

(X: H, NO_2; Y: H, Br, NO_2; py: Pyridine; dip: α, α′-Dipyridyl).

Although a hexa-coordinated octahedral configuration has been considered for bis-pyridine-bis-salicylaldehyde nickel by magnetochemical study[3], it is not definitely confirmed whether or not the copper atoms of these addition compounds are coordinated with six donors as yet. This paper presents some studies undertaken in order to investigate the structures of these addition compounds.

Spectrophotometric Studies.—Recently, Waters and Hall[4] have suggested that bis-salicylaldehyde copper(II) is solvated in coordinating solvents such as pyridine to give a penta- or hexa-coordinated copper(II) complex from the spectral change in various solvents. On the other hand, Charles[5] has shown that the spectra of some bis-*N*-*n*-alkylsalicylaldimine copper(II) in pyridine are similar to those in dioxane or toluene, although this is not the case with the corresponding nickel complexes. Therefore, he has concluded that no specific interaction (to form hexa-coordinated complexes) is present between the complexes and pyridine. However, the present author has observed that brown

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[1] H. B. Jonassen, R. E. Reeves and L. Sgal, *J. Am. Chem. Soc.*, 77, 2748 (1955); S. Kirschner, ibid., 78, 2372 (1956); D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 1956, 594; etc.

[2] Y. Muto, This Bulletin, 31, 56 (1958).

[3] F. Basolo and W. R. Matoush, *J. Am. Chem. Soc.*, 75, 5663 (1953).

[4] T. N. Waters and D. Hall, *J. Chem. Soc.*, 1959, 1200.

[5] R. G. Charles, *J. Am. Chem. Soc.*, 81, 1793 (1959).

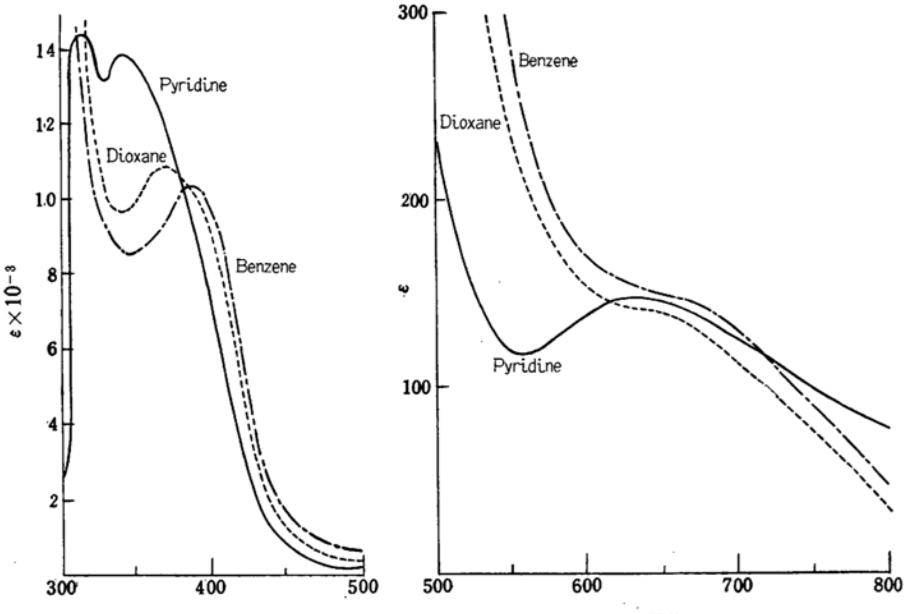


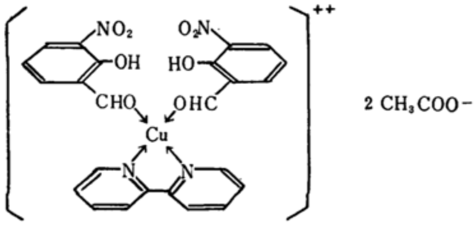
Fig. 1. Absorption spectra of bis-*N*-phenylsalicylaldimine copper(II).

bis-*N*-phenylsalicylaldimine copper(II) forms green crystals of a pyridinate having Formula II[2] and that its spectrum in pyridine is dissimilar to that in dioxane or benzene (Fig. 1). These facts confirm the formation of a hexa-coordination of the copper atom.

In addition, the author has observed that the absorption bands of bis-salicylaldehyde copper (II), a number of its derivatives, and bis-acetylacetone copper(II) in pyridine appear at longer wavelengths than those in dioxane (Figs. 2 and 3 and Table I). Probably, this indicates that the bands shift toward the longer wavelength side, owing to the formation of the hexa-coordinated copper(II) complexes in pyridine*.

Some Behaviors of the Addition Compounds. —Assuming that the addition compounds prepared in this study are hexa-coordinated copper-(II) complexes, the bond between the fifth or sixth donor and the copper atom should be weak relatively, as has been guessed from the fact that the usual coordination number of copper(II) is four. Actually, some of the pyridinates readily liberate pyridine. For example, bis-pyridine-bis-salicylaldehyde copper (II) lost pyridine gradually at room temperature. Also, the addition compounds with α, α′-dipyridyl were oxidized on heating in organic solvents such as ethanol to yield the derivatives of copper(II) monosalicylate[2], although α, α′-dipyridyl could be liberated from them with difficulty. This fact shows that probably the CHO → Cu bond is weak as compared with the N → Cu bond (in which N is a nitrogen atom of α, α′-dipyridyl). Namely, the CHO → Cu bond would be broken on heating in organic solvents, and then the aldehyde group would be oxidized, as benzaldehyde readily undergoes oxidation to benzoic acid in the presence of air.

Addition Compounds of α, α′-Dipyridyl-bis-3-nitrosalicylaldehyde Copper(II). — Among the addition compounds prepared in this study, only α, α′-dipyridyl-bis-3-nitrosalicylaldehyde copper(II) formed further addition compounds with chloroform, picric acid and acetic acid. Although no direct evidence has yet been afforded to elucidate the structures of these



III

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* It has been noticed by several investigators[6-8] that the absorption bands (from the near infrared to the near ultraviolet) of copper(II) complexes generally appear at longer wavelengths for hexa-coordinated complexes than for tetra-coordinated ones.

6) J. Bjerrum, C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1275 (1954).

7) H. Ito, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1395 (1956).

8) G. Gordon and R. K. Birdwhistell, *J. Am. Chem. Soc.*, **81**, 3567 (1959).

addition compounds by physical methods such as X-ray analysis, Formula III has been presumed for the acetate for the following reasons. First, it was observed that α, α′-dipyridyl-bis-3-nitrosalicylaldehyde copper(II) could not be oxidized by heating in organic solvents and that α, α′-dipyridyl and 3-nitrosalicylaldehyde could be liberated from this complex with difficulty by the action of acetic acid, although other addition compounds with α, α′-dipyridyl were decomposed to give α, α′-dipyridyl-copper(II)-acetate. From these results, it seems that CHO → Cu and N → Cu bonds are relatively strong. Secondly, it seems that the bond between copper and phenolic oxygen in α, α′-dipyridyl-bis-3-nitrosalicylaldehyde copper(II) has an ionic character to a considerable extent owing to the presence of a nitro and an aldehyde group at the ortho positions. Also, it has been observed that relatively strong acids such as picric acid or acetic acid add to the complex, while very weak acids such as phenol or cresol do not do so**. Therefore, it is possible that the complex forms a salt as shown in III.

TABLE I. ABSORPTION MAXIMA OF BIS-SALICYLALDEHYDE COPPER(II) DERIVATIVES IN THE VISIBLE REGION

	Solvents		
			(Addition compounds with α, α′-dipyridyl)
Substituent	Dioxane	Pyridine	Pyridine
5-Methyl	675 (1.71)	750 (2.04)	
None	670 (1.70)	740 (2.02)	700 (1.97)
5-Chloro	621 (1.62)	759 (1.95)	
5-Bromo	655 (1.93)	756 (2.27)	
3-Nitro-5-methyl	638 (1.65)	760 (1.92)	720 (1.97)
3-Nitro	670 (1.60)	710 (1.81)	704 (1.84)
5-Nitro	619 (?)	660 (2.45)	636 (2.40)
3,5-Dinitro	645 (?)	675 (2.37)	
Salicylaldehyde-ethylenedimine	576 (2.55)	602 (2.53)	
Bis-acetyl-acetone	612 (1.57)	654 (1.88)	

The values in parentheses are the logarithms of molar extinction coefficients (log ε) at the maxima. The value marked with a question mark could not be determined accurately owing to the slight solubility of the complex in dioxane.

Experimental

Spectrophotometric Measurements.—Bis-salicylaldehyde copper(II), its derivatives and bis-acetylacetone copper(II) were prepared by conventional methods. The addition compounds with α, α′-dipyridyl were prepared by the method described in the first paper[2] of this study. Although bis-*N*-phenylsalicylaldimine copper(II) was very soluble in various organic solvents, other complexes were soluble in pyridine, slightly soluble in dioxane, and soluble with difficulty in other common organic solvents.

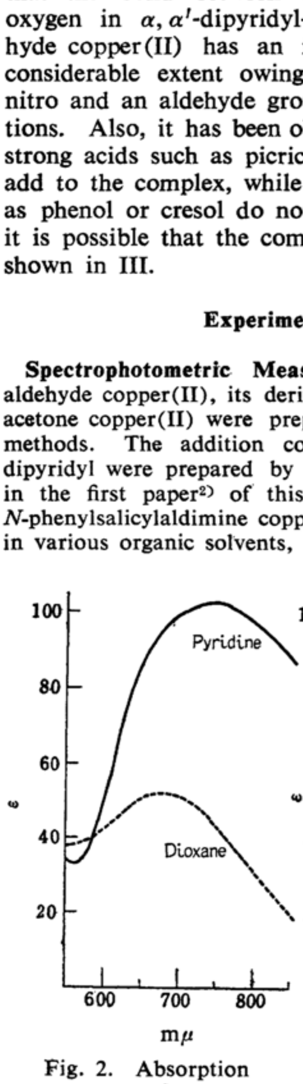

Fig. 2. Absorption spectra of bis-salicylaldehyde copper(II).

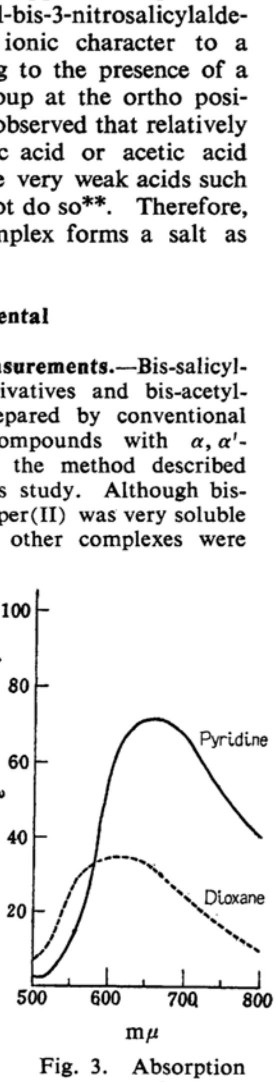

Fig. 3. Absorption spectra of bis-acetylacetone copper(II).

The absorption spectra were determined at 25 ±1°C with a Hitachi spectrophotometer (model EPU-2A) using 1 cm. quartz cells. The concentration of the complexes in solutions ranged from 5×10^{-5} to 3×10^{-3} mol. per liter depending upon the degree of absorption.

Preparation of additon compounds of α, α′-dipyridyl-bis-3-nitrosalicylaldehyde copper(II) with chloroform, picric acid, and acetic acid.—1) $Cu\cdot[O\cdot C_6H_3(NO_2)\cdot CHO]_2\cdot dip\cdot CHCl_3$.—α, α′-Dipyridyl-bis-3-nitrosalicylaldehyde copper(II) (yellow-brown crystals) (0.6 g.) was dissolved in chloroform (30 ml.) and the resulting brown solution was filtered. The filtrate was allowed to stand overnight in air at room temperature; meanwhile the addition compound crystallized in green prismatic crystals. It was purified by repeated recrystallization from chloroform.

Found: C, 44.67; H, 2.85; N, 8.17; Cu, 8.59; $CHCl_3$, 17.82. Calcd. for $C_{14}H_8O_8N_2\cdot Cu\cdot C_{10}H_8N_2\cdot CHCl_3$: C, 44.73; H, 2.55; N, 8.35; Cu, 8.56; $CHCl_3$, 17.78%.

Both α, α′ - dipyridyl - bis - 3 - nitrosalicylaldehyde cobalt(II) and the corresponding nickel complex prepared by a method of synthesis similar to that employed for the copper(II) complex formed no addition compound with chloroform.

The cobalt complex was isolated in the form of red crystals.

Found: N, 10.16; Co, 10.82. Calcd. for $C_{14}H_8O_8N_2\cdot Co\cdot C_{10}H_8N_2$; N, 10.24; Co, 10.77%.

The nickel complex was isolated in the form of orange crystals.

Found: N, 10.29; Ni, 10.56. Calcd. for $C_{14}H_8O_8N_2\cdot Ni\cdot C_{10}H_8N_2$; N, 10.24; Ni, 10.73%.

** Although it has been observed that *p*-nitrophenol add to the complex, the addition compound can not be isolated in the pure state.

2) $Cu \cdot [O \cdot C_6H_3(NO_2) \cdot CHO]_2 \cdot dip \cdot HO \cdot C_6H_2(NO_2)_3$.—$\alpha,\alpha'$-Dipyridyl-bis-3-nitrosalicylaldehyde copper(II) (0.3 g.) was added to 50 ml. of ether containing 0.2 g. of picric acid. The mixture was refluxed on a water bath for half an hour, meanwhile the addition compound crystallized in green prismatic crystals. The separated crystals were washed with ether repeatedly and then dried in a desiccator over sulfuric acid.

Found: C, 46.40; H, 2.71; N, 12.47; Cu, 8.16. Calcd. for $C_{14}H_8O_8N_2 \cdot Cu \cdot C_{10}H_8N_2 \cdot C_6H_3O_7N_3$; C, 46.13; N, 12.55; Cu, 8.15%.

3) $Cu \cdot [O \cdot C_6H_3(NO_2) \cdot CHO]_2 \cdot dip \cdot (CH_3COOH)_2$.—$\alpha,\alpha'$-Dipyridyl-bis-3-nitrosalicylaldehyde copper(II) (0.6 g.) was dissolved in a mixture of ether (20 ml.) and acetic acid (3 ml.) and the resulting solution was filtered. When 30 ml. of ether was added to the filtrate, the addition compound precipitated in green prismatic crystals. The crystals were separated, washed with ether repeatedly, and then dried in a vacuum desiccator over sulfuric acid.

Found: C, 49.76; H, 3.89; N, 8.23; Cu, 9.26; CH_3COOH, 17.73. Calcd. for $C_{14}H_8O_8N_2 \cdot Cu \cdot C_{10}H_8N_2 \cdot C_4H_8O_4$: C, 50.04; H, 3.60; N, 8.34; Cu, 9.45; CH_3COOH, 17.87%.

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