Some Addition Compounds of Salicylaldehyde-ethylenediimine-copper. VI[1]. *The Absorption Spectra of 5, 5′-Disubstituted Salicylaldehyde-ethylenediimine-coppers*

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It had been reported previously that the positions of the absorption maxima of the spectra of salicylaldehyde-ethylenediimine-copper were shifted in regular ways according to the nature of the solvents in which the absorption spectra were measured[2]. Now the absorption spectra of 5, 5′-dichloro-[2], 5, 5′-dibromo-, 5, 5′-diiodo-salicylaldehyde-ethylenediimine-coppers[3] have been measured in various solvents, and some close relations have been observed between the position of the absorption maxima of band I and band II[4] of these chelates and their tendencies to form addition compounds with the solvents.

Measurement and Results

The absorption spectra were measured with a Hitachi EPU 2A spectrophotometer (cell depth 1.0 cm.). All solvents were purified according to the method of Weissberger[5]. The results are listed in Table I.

Discussion

Band I.—Although many discussions[6] have been presented by different authors about the origin of the visible band of the metal chelates, satisfactory experimental evidence for them have not yet been obtained. It is now frequently assumed, however, that the greatest factor leading to this absorption is the vibration of the non-bonding electron of the metal ion.

Martell and Ueno[7] measured the absorption spectra of the metal chelates of bisacetylacetone-ethylenediimine and its derivatives and found that the band I of copper chelates which appeared between 540~575 mμ is the characteristic absorption of the copper ion. Analogous observations had previously been reported by Sone[8] about the absorption spectra of the bidentate chelates.

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[1] Bissalicylaldehyde-ethylenediimine-copper. Part V. *J. Chem. Soc. Japan, Pure. Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1013 (1960).

[2] T. Tanaka, *J. Am. Chem. Soc.*, **80**, 4108 (1958).

[3] T. Tanaka, This Bulletin, **33**, 259 (1960).

[4] T. Tsumaki. ibid., **13**, 252 (1938) ; A. v. Kiss, P. Csokan and G. Nyiri., *Z. physik. Chem., Abt. A.*, **190**, 65 (1942).

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

[6] Cf., for example, L. Pauling, *J. Am. Chem. Soc.*, **53**, 1367 (1931) : A. Mead, *Trans. Faraday. Soc.*, **30**, 1052 (1934).

[7] K. Ueno and A. E. Martell, *J. Phys. Chem.*, **61**, 257 (1957).

[8] K. Sone, *J. Am. Chem.* Soc., **75**, 5207 (1953).

TABLE I. THE ABSORPTION SPECTRA OF SALICYLALDEHYDE-ETHYLENEDIIMINE-COPPER DERIVATIVES

Solvent	Substituent	Absorption maximum in $m\mu$ ($\log \varepsilon$), shift in $m\mu$					
		Band I	Shift	Band II	Shift	Band III	Shift
Benzene	5,5′-H	572(2.34)[d]		372(3.68)[d]		276(4.66)	
	5,5′-Cl	575(1.88)		379(3.49)		276(3.74)	
	5,5′-Br	566(2.01)		379(3.51)		275(3.87)	
	5,5′-I	549(2.30)		379∼381(3.96)[b]		276(4.42)	
Pyridine	5,5′-H	603(2.67)[d]	+31[c]	372(4.27)[d]	0	299.5(3.60)	+23.5
	5,5′-Cl	593(2.46)	+18[c]	379(4.15)	0	299(3.72)	+23
	5,5′-Br	589(2.51)	+23	379(4.54)	0	301(3.29)	+26
	5,5′-I	594(2.44)	+45	379(3.71)	0	300(3.54)	+24
Chloroform	5,5′-H	564(2.55)[d]	−8	365∼370(4.01)[d]	−(2∼7)	276(4.47) 245(4.59)	0 −31
	5,5′-Cl	552(2.41)	−23	375∼377(2.72)	−(2∼4)	245(4.32)	−31
	5,5′-Br	553(2.58)	−13	374∼379(4.35)	−(0∼5)	242∼246(5.03)	−(29∼33)
	5,5′-I	544(2.42)	−5	377(3.75)	−2	244.5(4.48)	−31.5
Propionic acid	5,5′-H	560(2.17)[d]	−12	350(3.89)[d]	−22	271(4.83)	−5
	5,5′-Cl	554(2.34)	−21	359(3.40)	−20	247(4.37)	−29
	5,5′-Br	549(2.34)	−17	357∼361(3.71)	−(18∼22)	255∼258(4.30)	−(17∼20)
	5,5′-I	548(2.34)	−1	361(3.27)	−18	249(3.96)	−27
Propionic acid-Benzene[a]	5,5′-H	559(2.30)[d]	−13	356(4.30)[d]	−16	276(4.38)	0
	5,5′-Cl	557(2.32)	−18	368(3.94)	−11	276(4.27)	0
	5,5′-Br	559(2.44)	−7	365∼370(4.21)	−(9∼14)	275(4.61)	0
	5,5′-I	555(2.36)	+6	370(4.11)	−9	276(4.63)	0
Phenol-Benzene[a]	5,5′-H	550(2.38)[d]	−22	358∼359(4.19)[d]	−(13∼14)	293(3.80)	+17
	5,5′-Cl	552(2.38)	−23	368(3.89)	−11	293(3.80)	+17
	5,5′-Br	553(2.48)	−13	369(3.82)	−10	293(3.77)	+18
	5,5′-I	542(2.46)	−7	369(3.60)	−10	293(3.66)	+17

a 3 M (acid or phenol) solution in benzene.
b 379 $m\mu$ was taken as the standard.
c + indicates the red shift and − the blue shift.
d These values were previously reported (cf. Ref. 2).

TABLE II. ADDITION COMPOUNDS OF SALICYLALDEHYDE-ETHYLENEDIIMINE-COPPER DERIVATIVES[2,3]

Substituent	Addition compound			
	Pyridine	Propionic acid	Chloroform	Phenol
5,5′-H	—	Stable	—	Stable
5,5′-Cl	—	—	Least stable	Less stable
5,5′-Br	—	—	Less stable	Stable
5,5′-I	—	Stable	Stable	Stable

Calvin et al.[9] reported that band I of the copper chelates of bisacetylacetone and its 3-ethyl variant is composed of a set of three Gaussian components whose positions and intensities were shown to depend primarily upon solvent basicity; these component bands were identified with the transitions of the 3d electrons of the copper ion predicted from the crystal field and molecular orbital theories.

In this report, it is examined whether there are any relations between the tendencies of 5, 5′-dichloro-, 5, 5′-dibromo- and 5, 5′-diiodo-salicylaldehyde-ethylenediimine-coppers to form addition compounds with propionic acid, phenol and chloroform and the positions of band I of these chelates observed in these solvents.

The wavelengths of the absorption maxima of band I of these chelates in benzene solutions, as listed in Table I, increase in the order

$$5,5'\text{-I} < 5,5'\text{-Br} < 5,5'\text{-Cl}$$

which is the order of decreasing basicity[10];

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[9] R. L. Belford, M. Calvin and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).

[10] R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. & Nuclear Chem.*, **2**, 11 (1956).

that of the unsubstituted one lies between those of 5, 5'-dichloro- and 5, 5'-dibromo-derivatives, the order is

$$5, 5'\text{-I} < 5, 5'\text{-Br} < 5, 5'\text{-H} < 5, 5'\text{-Cl}$$

The extinction coefficients of band I as well as those of band II and band III of these chelates observed in the same solvent decrease in the order

$$5, 5'\text{-I} > 5, 5'\text{-Br} > 5, 5'\text{-Cl}$$

The shifts listed in Table I were calculated as the deviations of the wavelengths of the absorption maxima measured in various solvents from those measured in benzene solutions.

In the pyridine solutions, red shifts of the absorption maxima of the band I were observed of these chelates. The magnitudes of the red shifts decrease in the order

$$5, 5'\text{-I} > 5, 5'\text{-H} > 5, 5'\text{-Br} > 5, 5'\text{-Cl}$$

On the other hand, in chloroform and propionic acid solutions, blue shifts were observed. The magnitudes of the blue shifts increase in the order

$$5, 5'\text{-I} < 5, 5'\text{-H} < 5, 5'\text{-Br} < 5, 5'\text{-Cl}$$

that is, the chelates which are characterized by the larger red shifts in pyridine solutions are those characterized by the smaller blue shifts in chloroform and propionic acid solutions.

It can be seen that these orders are the same as that of the tendency of the formation of the addition compounds which was reported previously[3)].

In the cases of the propionic acid-benzene and of the phenol-benzene solutions, the order of the shifts is somewhat different from those discussed above; it is the same as that of the wavelengths of these chelates in benzene solutions. The blue shifts increase in the order

$$5, 5'\text{-I} < 5, 5'\text{-Br} < 5, 5'\text{-H} < 5, 5'\text{-Cl}$$

It is remarkable that a red shift is observed in the case of 5, 5'-diiodo-chelate in the propionic acid-benzene solution in contrast with the blue shifts of 5, 5'-dichloro- and 5, 5'-dibromo-chelates.

These results indicate that the energy changes of the 3d electrons which may be induced both by the ligands and the solvents are closely related to the tendency of the formation of the addition compounds. The circumstances are, however, somewhat more complicated in the case of the mixed solvents containing benzene and require further examination. It is also important to inquire whether there are any relations between the stabilities of the addition compounds of these chelates with solvents and the wavelengths of the absorption maxima of band I of the chelates in the respective solvents.

In the chloroform solutions, the absorption maxima are 544 mμ for 5, 5'-diiodo-chelate and 553 and 552 mμ for 5, 5'-dibromo, 5, 5'-dichloro-chelates, corresponding to the formation of stable and less stable addition compounds respectively, and 564 mμ for the unsubstituted chelate of which the addition compound cannot be isolated.

On the other hand, band III of the unsubstituted chelate in a chloroform solution consists of two maxima, i. e., a band at 245 mμ which seems to originate from the unstable addition compound of the chelate with chloroform and a band at 276 mμ which seems to originate from the original chelate; the former is analogous to band III of the substituted chelates in chloroform, while the latter is analogous to the absorption maxima of the unsubstituted chelate in a benzene solution. Therefore, the chelate is considered to exist in the chloroform solution as an equilibrium mixture of the original chelate with the unstable addition compound with chloroform.

In the phenol-benzene solutions, the maxima are 542 mμ for 5, 5'-diiodo-chelate corresponding to the formation of a stable addition compound with phenol, 550 mμ for an unsubstituted one, and 553 and 552 mμ for 5, 5'-dibromo- and 5, 5'-dichloro-chelates corresponding to less stable addition compounds.

These results seem to indicate that the shorter the wavelength of the absorption maximum of a chelate observed in a solvent, the greater the stability of the addition compound of the chelate with the solvent.

Band II.—In contrast with those of band I and band III, the wavelengths of the absorption maxima of band II in the spectra of 5, 5'-dichloro-, 5,5'-dibromo- and 5,5'-diiodo-chelates were found at 379 mμ in both benzene and pyridine solutions.

The flat maximum of 5, 5'-diiodo-chelate in benzene from 379 to 381 mμ was an abnormal case of which no appropriate explanation can be made at present.

The blue shifts of 2 mμ for 5, 5'-diiodo-chelate, 0∼5 mμ for 5, 5'-dibromo-chelate and 2∼4 mμ for 5, 5'-dichloro-chelate in the chloroform solutions, corresponding to stable, less stable and least stable addition compounds of these chelates with chloroform respectively, represent a series. Analogous series of the blue shifts of the wavelength of the absorption maxima of band II were observed in the propionic acid solutions as well as in the propionic acid-benzene solutions. The shifts in propionic acid solutions are, respectively, 18 mμ for 5, 5'-diiodo-chelate which can form an addition compound with propionic acid, and 18∼22 and 20 mμ for 5, 5′-dibromo- and 5, 5′-dichloro-chelates which can not form addition compounds with propionic acid; those in propionic acid-benzene solutions are 9 mμ for 5, 5′-diiodo-, 9∼14 mμ for 5, 5′-dibromo- and 11 mμ for 5, 5′-dichloro-chelates. In the phenol-benzene solutions, the blue shifts are 10 mμ for 5, 5′-diiodo- and 5, 5′-dibromo-chelates and 11 mμ for 5, 5′-dichloro-chelates, all of which can form addition compounds with phenol.

From these results, it is assumed that the smallest shifts for 5, 5′-diiodo-chelate observed in chloroform as well as in propionic acid and in propionic acid-benzene solutions are related to the formation of the stable addition compounds of this chelate with these solvents, and the larger shifts for 5, 5′-dichloro-chelate correspond to the formation of unstable associated structures. The flat maxima of band II of 5, 5′-dibromo-chelate in these solvents, which are characterized by blue shifts ranging from the largest to the smallest values may be due to the properties of this chelate which are intermediate between those of 5, 5′-diiodo- and 5, 5′-dichloro-chelates.

It is also important to notice that 5, 5′-halogen substituents in comparison with that of the unsubstituted chelate, produce a marked influence on the wavelengths of band II.

Band III.—Some different orders are observed of the absorption maxima of band III of these chelates. Larger shifts of the wavelengths of the absorption maxima of 5, 5′-dibromo-chelate than those of the others were observed in the pyridine as well as in the phenol-benzene solutions. A smaller blue shift of 5, 5′-dibromo-chelate than those of the others was also observed in the propionic acid solution, while a flat maximum of 5, 5′-dibromo-chelate, with a blue shift ranging from 29 to 33 mμ in chloroform solution, was contrasted with those of the blue shifts of 31 mμ of 5, 5′-dichloro-chelate and 31.5 mμ of 5, 5′-diiodo-chelate in the same solvent. No shifts of the band III of these three chelates were observed in the propionic acid-benzene solutions.

It is important to notice that band III of the unsubstituted chelate in the chloroform solution consists of two maxima (cf. the discussions for band I).

From these results, it is supposed that 5, 5′-halogen substituents do not exert a marked influence on the origin of band III[7,11].

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[11] T. Tsumaki and R. Tsuchida, This Bulletin, 13, 527 (1938).