Some Addition Compounds of Salicylaldehyde-ethylenediimine-copper. I

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Among the addition compounds of the metal chelates of salicylaldehyde-ethylenediimine, several are well studied[1] because of their theoretical and practical importance. But most of them are the complexes of iron and cobalt which can form stable chelates not only in square but also in octahedral configurations.

Pfeiffer and others[2] observed that the green crystals of salicylaldehyde-ethylenediimine-copper gave a purple solution when dissolved in chloroform or in glacial acetic acid, and a green solution in pyridine. But they made no detailed studies about it.

The author suspected that this hypsochromic effect in the visible region must be due to the formation of the addition compounds, and succeeded in isolating some new addition compounds of salicylaldehyde-ethylenediimine-copper, of which the addition compound was hitherto unknown. Although the copper complex, crystallized from chloroform solution gives green leaflets of the original complex, an addition compound of purple needles was obtained when the saturated solution of salicylaldehyde-ethylenediimine-copper in acetic acid was concentrated under vacuum at room temperature. Further, some addition compounds with phenol were also isolated in crystalline state.

The addition compounds, salicylaldehyde-ethylenediimine-copper-acetic acid and salicylaldehyde-ethylenediimine-copper-phenol have the formulae $C_{16}H_{14}N_2O_2Cu \cdot C_2H_4O_2$ and $C_{16}H_{14}N_2O_2Cu \cdot C_6H_6O$ respectively. These compounds return to the original green complex salt, rather slowly when in contact with water and rapidly when in contact with alcohols.

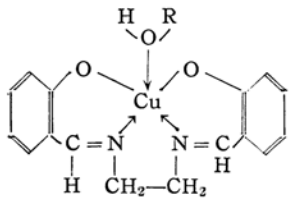
The remarkable colour changes and the reversible additions and eliminations of acid and phenol must be concerned with the central metal copper, and the following three possible structures can be considered for such addition compounds.

By analogy (I) is considered to be valid in the ordinary addition compounds. But pyridine, ethyl acetate, anisole and anilline can not isolate addition compound of any stability, and in such an acidic conditions as we are now concerned with (II) and (III),.....which can be considered as the intermediates of acid degradation of the complex salt....., would be more probable and proton transfer at least would be considered to be necessary.

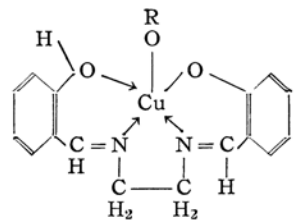
Among *o*-nitrophenol, *p*-nitrophenol, and picric acid, the latter two can form addition compounds, but *o*-nitrophenol can not form such an addition compound.

The addition compound with picric acid is stable and can be recrystallized from alcohol in brown crystals. This differs from the addition compounds of ordinary acids and phenols. Because of the steric hindrance of ortho substituted nitro groups, covalently linked structure (II) is not considered for the picric acid addition compound, but the ionic structure (III) is assigned to it. And consequently the structure (II) may be assigned to the ordinary purple addition compounds.

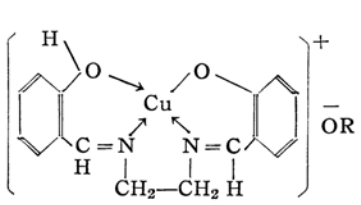
Copper complexes are known to have a



(I)



(II)



(III) R=CH_3–CO, C_6H_5

square configuration[3] around copper and this configuration was justified by Pauling[4] by means of the hybridization of dsp_2 orbitals,

1) T. Tsumaki, *J. Chem. Soc. Japan*, 58, 1258 (1937). T. Tsumaki and Z. Endo, *J. Chem. Soc. Japan*, 64, 31 (1943). M. Calvin et al., *J. Am. Chem. Soc.*, 68, 2254, 2257, 2263 (1946).

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

3) M. v. Stackelberg, *Z. anorg. Chem.*, 253, 136 (1947)

4) L. Pauling, *J. Am. Chem. Soc.*, 53, 1367 (1931).

but some complexes which have penta-covalent pyramidal structure[5,*] as in (I) and (II), are also reported.

In chloroform solution, the complex is supposed to assume such a structure as to contain intermediate weak coordinate link[**]. Anisole and anilline also produce purple coloration with the complex. 5-Nitrosalicylaldehyde-ethylenediimine-copper also forms addition compound with acetic acid or phenol, but 5-chlorosalicylaldehyde-ethylenediimine-copper does not form an addition compound with acetic acid, but forms a brick red addition compound with phenol, though this is not obtained in the pure state, because of its low solubility in any non-basic organic solvents.

Experimental

Salicylaldehyde-ethylenediimine-copper-acetic Acid

The saturated solution of salicylaldehyde-ethylenediimine-copper in glacial acetic acid is concentrated to its half volume under vacuum at room temperature. Large violet needles separate, which are filtered, and freed from acetic acid in vacuum desiccator on calcium chloride. This addition compound is unstable, and decomposed completely into the original complex on exposure to air overnight.

Water, methyl alcohol, ethyl alcohol, propyl alcohol, aniline and pyridine decompose this addition compound rapidly.

Anal. Found; C, 55.15; H, 4.56; N, 7.11; Cu, 16.45. Calcd. for $C_{18}H_{18}N_2O_4Cu$: C, 55.45; H, 4.65; N, 7.19; Cu, 16.30.

Salicylaldehyde-ethylenediimine-copper-phenol

The mixture of 1 mol. of salicylaldehyde-ethylenediimine-copper and 1.1 mol. of phenol is warmed above the melting point of the latter, immediate formation of addition compound occurs. The mass is washed with chloroform-benzene (1.10) to remove the excess of phenol.

The addition compound is stable in non-basic solvent, also in water, but is decomposed rapidly by alcohols. Fairly soluble in chloroform, sparingly soluble in benzene. m. p. 125°.

Anal. Found: C, 62.69; H, 4.77; N, 6.30; Cu, 14.50. Calcd. for $C_{22}H_{20}N_2O_3Cu$: C, 62.31; H, 4.75; N, 6.61; Cu, 14.99.

Salicylaldehyde-ethlenediimine-copper-p-nitrophenol

The mixture of 1 mol. of salicylaldehyde-ethylenediimine-copper and 1.1 mol. of *p*-nitrophenol is warmed above the melting point of the latter. Purple needles are formed immediately. The mass is dissolved in chloroform, and precipitated by the addition of benzene. The precipitates are recystallized from chloroform solution. The addition compound is obtained in purple needles. m.p. 225°.

Anal. Found: C, 55.65; H, 4.56; N, 9.16; Cu, 13.00. Calcd. for $C_{22}H_{19}N_3O_5Cu$: C, 56.34; H, 4.08; N, 8.96; Cu, 13.55.

Salicylaldehyde-ethylenediimine-copper-picric acid

A suspension of 1 mol. of salicylaldehyde-ethylenediimine-copper and 2 mol. of picric acid in chloroform is stirred for two hours at room temperature. The brown precipitates separate, which are filtered, washed with benzene and recrystallized from 80% alcohol. The brown needles, which contain 1 mol. water are stable in usual organic solvents. Stable in usual organic solvents.

Anal. Found: C, 45.62; H, 3.28; N, 12.51; Cu, 10.55. Calcd. for $C_{22}H_{17}N_5O_9Cu \cdot H_2O$: C, 45.79; H, 3.32; N, 12.14; Cu, 11.01.

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5) cf. M. Calvin and E. Martell, "Metal Chelate Compounds", Prentice-Hall (1952), pp. 113, 243, 286.

* Tetrahedral structure is also of some contribution in some cases.

cf. G. Kimball, *J. Chem. Phys.*, 8, 188 (1940); R. Hultgren, *Phys., Rev.*, 40, 891 (1932); H. Kuhn, *J. Phys.*, 16, 727 (1948); P. Pfeiffer, *Angew. Chem.*, 53, 93 (1940).

If $-O\rightarrow Cu$ coordination is weak, (II) would be irregular tetrahedral configuration and the mechanism of the addition compound formation would be bimolecular nucleophilic substitution of the protonated complex.

** This will be indicated by the special shifts of absorption bands as discussed in II of this series.