Coördinate Valency Rings. XXIV.[1] *On Some Inner Complex Ferric Salts of Hydrosalicylamide and its Derivatives*[*]

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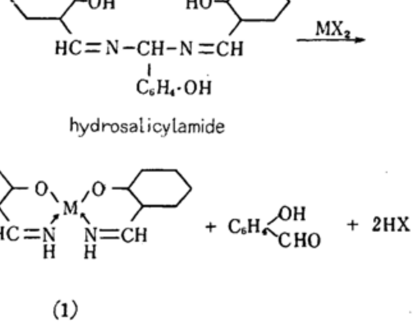
It is well known that salicylaldehyde reacts readily with ammonia in an alcoholic solution to form hydrosalicylamide, which consists of 3 molecules of salicylaldehyde and 2 molecules of ammonia, involving elimination of 3 molecules of water. When hydrosalicylamide is treated with divalent metallic salts, such as



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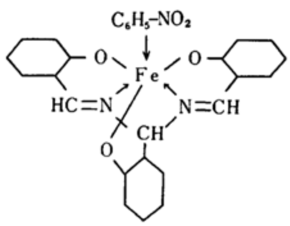
[1] Part XXIII: T. Tsumaki, K. Katsuta and S. Okada, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1086 (1957).

[*] Presented at the Joint Meeting of the Chugoku-Shikoku Branch and Kyushu Branch of the Chemical Society of Japan, Matsuyama, June 7, 1958.

copper or nickel salts, metal chelates of salicylaldimine (formula 1) instead of those of hydrosalicylamide are obtained[2].

In the chelate-forming reactions, therefore, hydrosalicylamide splits by metallic salts giving one molecule of salicylaldehyde.

An attempt was made in 1934, by one of the authors[3], to obtain an analogous ferrous complex salt, that is, bis-salicylaldimine-iron(II) by the reaction between hydrosalicylamide and ferrous sulfate. But the obtained chelate recrystallized from nitrobenzene was trisalicylaldehyde-diimine-iron(III), which contained one molecule of nitrobenzene coördinated to iron atom (formula 2). During the reaction, therefore, ferrous complex salt was oxidized to ferric by atmospheric oxygen.



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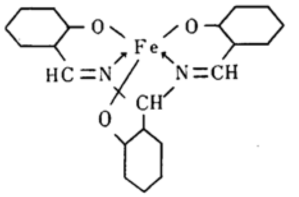

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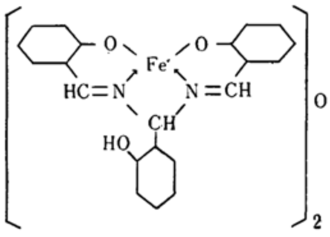

(4)

Later, by using ammonium ferric sulfate, instead of ferrous sulfate, the same product was obtained as had been expected[4].

In the above-mentioned reactions, the main product, before recrystallization from nitrobenzene, consists of reddish brown powder. In the present paper are described the method of preparation of this compound in pure state and the comfirmation of its chemical structure. The structure of the compound, in recognition of the structure of nitrobenzene-containing chelate indicated by formula 2, is considered as a rarely known penta-coördinated ferric complex (formula 3). Besides formula 3, another formula, 4, may be taken into consideration for the ferric complex, on the basis of the results of elementary analysis and of the route of preparation of the complex. Of these two formulae, the latter should be excluded for reasons described below.

1) The complex salt does not react with diazomethane. The presence of a phenolic hydroxyl group must be denied.

2) It is known that the ferric complexes of oxide-form, for example, bis-salicylaldehyde-ethylenediimine-ferric oxide, react with a number of weak organic acids to give their salts (formula 5)[5]. Our complex, however, does not show such behavior.

3) If the hydroxyl group of the central salicylidene group does not take part in the complex formation as in the case of formula 4, the synthesis of a complex salt having formula 6, which has a benzylidene group in place of a salicylidene group in formula 4, may be possible by the action of a ferric salt on 2, 2′-dihydroxyhydrobenzamide. The complex salt of formula 6, however, could not be obtained by such attempts, and only a complex salt of hydrosalicylamide having formula 3 was obtained. Therefore, it can be considered that benzaldehyde splits off from the ligand and salicylaldehyde takes its place in the course of the reaction. This fact indicates that three hydroxyl groups of hydrosalicylamide may all be used for the complex formation.

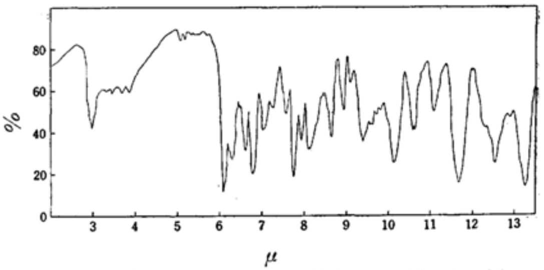

Fig. 1. Infrared spectrum of hydrosalicylamide.

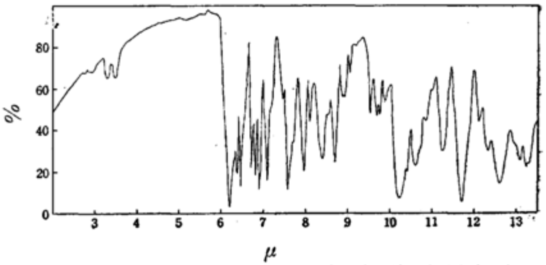

Fig. 2. Infrared spectrum of trisalicylaldehyd-diimine-iron(III).

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[2] P. Pfeiffer, E. Buchholz and O. Bauer, *J. prakt. Chem.*, **129**, 163 (1931).

[3] T. Tsumaki, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **55**, 1245 (1934).

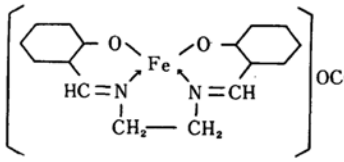
[4] T. Tsumaki, ibid., **56**, 1329 (1935).

[5] P. Pfeiffer, E. Breith, E. Lübbe and T. Tsumaki, *Ann.* **503**, 84 (1933). T. Tsumaki, M. Kuramoto, Y. Nakaishi and S. Suzuki, *Reports of Faculty of Science, Kyushu Univ., Chem. Sec.*, **1**, 63 (1950).

4) The infrared spectra indicate the absence of phenolic hydroxyl groups (Figs. 1 and 2).

Because of the above-mentioned experimental facts, the pentadentate formula 3 should be given to the ferric complex in question and the structure (formula 2) of its nitrobenzene-containing adduct has been proved to be correct.

For some of the so-called tri-coördinated copper complexes, the presence of dimeric molecules has been suggested because of their abnormally low magnetic moments[6]. In the case of our pentadentate ferric complex, it has been shown by the measurement of magnetic susceptibilities that it has a normal magnetic moment (5.82 B. M.) and O–Fe bonds are essentially ionic. Therefore, the complex does not exist in the form of dimers.



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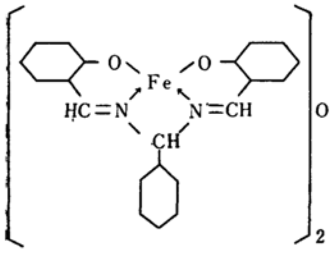

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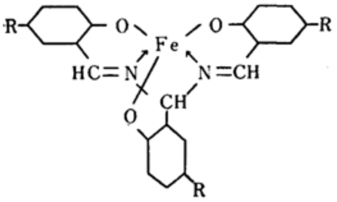

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As the penta-coördinated complex is coördinatively unsaturated, it will be expected that the complex will have a strong tendency to become a hexa-coördinated one, by the addition of a ligand molecule. The nitrobenzene adduct is a good example. Further, we succeeded in obtaining some such adducts, which contain pyridine, quinoline, bromobenzene, α-chloronaphthalene, ethylene chloride and methyl benzoate. Each of the ligand molecules, except ethylene chloride, is bound firmly to the complex. The expelling of them is completed only by heating the adducts at 150~170°C for 8~10 hr. under 10 mmHg. It is well known that tertiary amines such as pyridine or quinoline enter very often into the complexes as ligands, but the examples of adducts which contain nitro-compounds or halogenated hydrocarbons have been rarely known.

Starting from benzene-substituted methyl-, chloro-, bromo- and nitro-derivatives of hydrosalicylamide, corresponding penta-coördinated iron complexes and their hexa-coödinated adducts were obtained (formula 7). In the case of methyl derivative, however, it formed no addition compound.

All these complexes decompose hydrogen peroxide catalytically and for that reason show strong chemi-luminescence in the presence of luminol in an alkaline solution.

Experimental

Trisalicylaldehyde - diimine - iron (III). — Hydrosalicylamide (2 g.) is dissolved in absolute alcohol (300 cc.) in a three necked round-bottomed flask (500 cc.) fitted with a glass filter, a stirrer and a reflux condenser protected by calcium chloride. The solution is stirred and heated to 70~75°C on a water bath. A solution of anhydrous ferric chloride (0.6 g.) in absolute alcohol (50 cc.) is allowed to flow into the flask through a glass filter. The solution changes at once from yellow to orange red. After about two hours the reaction product is filtered off, washed with hot alcohol several times and dried at 90°C. Yield 1.5 g., black needles.

Found: C. 62.71; H, 4.18; N, 6.76; Fe, 13.78. Calcd. for $C_{21}H_{15}N_2O_3Fe$: C, 63.18; H, 3.78; N, 7.02; Fe, 13.99%.

Reaction between 2, 2′-Dihydroxyhydrobenzamide and Ferric Chloride.—The reaction is carried out by essentially the same method as described above, using 2, 2′-dihydroxyhydrobenzamide and ferric chloride. The resulting black crystals are recrystallized from nitrobenzene.

Found: N, 8.25; Fe, 10.52; drying loss, 23.66. Calcd. for $C_{21}H_{15}N_2O_3Fe \cdot C_6H_5NO_2$: N, 8.05; Fe, 10.69; nitrobenzene, 23.57%.

Since the description in the literature regarding 2, 2′-dihydroxyhydrobenzamide had been only briefly given in the U. S. patent[7], a sample synthesized by the authors was ascertained by elementary analysis. m. p. 117°C. Pale yellow needles.

Found: C, 76.48; H, 5.52; N, 8.35. Calcd. for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48%.

Magnetic Susceptibility.—The magnetic susceptibilities of trisalicylaldehyde-diimine-iron (III) and its nitrobenzene adduct were measured by the Curie method at room temperature (17°C). Cupric sulfate pentahydrate (further purified by the recrystallization of an extra pure reagent thrice from water) was used as the standard sample. The results are presented in Table I, where χ is the magnetic susceptibility per gram of the complex.

Neglecting the diamagnetic contribution of the ligand and assuming the validity of Curie-Langevin's law, the effective magnetic moments μ per one mole of the complex were calculated (see also Table I).

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[6] M. Kishita, Y. Muto and M. Kubo, *Austral. J. Chem.*, **10**, 386 (1957).

[7] J. A. Chenicek, U. S. Pat. 2,533,205 (1950).

TABLE I.

	χ (c. g. s., e. m. u.)	μ (B. M.)
Trisalicylaldehyde-diimine-iron(III) + nitrobenzene	28.5×10^{-6}	5.90
Trisalicylaldehyde-diimine-iron(III)	36.3×10^{-6}	5.82

The theoretical moment of iron(III) (calculated from "spin-only" formula) is 1.73 B. M. for covalent bonds and 5.92 for the ionic ones.

Infrared Spectra.—They were taken in a hexachlorobutadiene mull, with an Oyo-Koken double beam instrument equipped with a sodium chloride prism (Figs. 1 and 2).

Addition Compounds of Trisalicylaldehyde-diimine-iron(III).—These compounds were prepared by the recrystallization of trisalicylaldehyde-diimine-iron (III) from various organic solvents. They are dried in a vacuum desiccator, because the coördinated solvent molecules are partially removed on heating or by washing with alcohol. All of them form black plates and their appearance or colors are almost unaltered by desolvation.

Trisalicylaldehyde-diimine-iron(III) + Pyridine.

Found: N, 8.88; Fe, 11.51; drying loss, 16.90. Calcd. for $C_{21}H_{15}N_2O_3Fe\cdot C_5H_5N$: N, 8.79; Fe, 11.68; pyridine, 16.54%.

Trisalicylaldehyde-diimine-iron(III) + Quinoline.

Found: C, 67.94; H, 4.46; N, 7.82; Fe, 10.42; drying loss, 24.63. Calcd. for $C_{21}H_{15}N_2O_3Fe\cdot C_9H_7N$: C, 68.18; H, 4.17; N, 7.95; Fe, 10.57; quinoline, 24.43%.

Trisalicylaldehyde-diimine-iron(III) + α-Chloronaphthalene.

Found: C, 65.95; H, 4.26; N, 4.78; Fe, 9.60. Calcd. for $C_{21}H_{15}N_2O_3Fe\cdot C_{10}H_7Cl$: C, 66.27; H, 3.95; N, 4.99; Fe, 9.33%.

Trisalicylaldehyde-diimine-iron(III) + Ethylene Chloride.

Found: C, 57.35; H, 4.13; N, 5.72; Cl, 12.35; Fe, 11.65; drying loss, 16.40. Calcd. for $C_{21}H_{15}N_2O_3Fe\cdot 0.8\ C_2H_4Cl_2$: C, 57.12; H, 3.86; N, 5.90; Cl, 11.94; ethylene chloride, 16.00%. The complex salt desolvates at room temperature. The analytical results shown above are the average values of several analyses.

Trisalicylaldehyde-diimine-iron(III) + Methyl Benzoate.

Found: Fe, 10.32; drying loss, 25.92. Calcd. for $C_{21}H_{15}N_2O_3Fe\cdot C_8H_8O_2$: Fe, 10.43; methyl benzoate, 25.43%.

Tri(5-substituted-salicylaldehyde)-diimine-iron-(III).

Tri(5-methylsalicylaldehyde)-diimine-iron(III).—By a method similar to that mentioned above for the synthesis of trisalicylaldehyde-diimine-iron(III), a solution of ferric chloride (0.4 g.) in absolute alcohol (10 cc.) is added to a solution of 5, 5′, 5″-trimethylhydrosalicylamide (1 g.) in absolute alcohol (70 cc.). But in this case, in order to avoid the decomposition of the ligand at high temperature, the reaction is carried out at 45∼50°C. The product was purified by reprecipitation from pyridine with water. Black needles.

Found: C, 64.87; H, 4.98; N, 6.36; Fe, 12.40. Calcd. for $C_{24}H_{21}N_2O_3Fe$: C, 65.32; H, 4.80; N, 6.35; Fe, 12.66%.

Tri(5-bromosalicylaldehyde)-diimine-iron(III) + Nitrobenzene.—A solution of 5, 5′, 5″-tribromohydrosalicylamide (1 g.) (or 5-bromosalicyladehyde and ammonia) in alcohol (30 cc.) is warmed on a water bath and a solution of ammonium ferric sulfate (dodecahydrate; 0.7 g.) in water (7 cc.) is added to it. After about half an hour, the black brown precipitates are filtered off, washed with hot alcohol and dried on a tone plate. Yield 0.7 g.

The powder is recrystallized from nitrobenzene to give the black plates which are dried in vacuo.

Found: C, 42.87; H, 2.48; N, 5.37; Fe, 7.27; drying loss, 16.17. Calcd. for $C_{21}H_{12}N_2O_3Br_3Fe\cdot C_6H_5NO_2$: C, 42.67; H, 2.25; N, 5.37; Fe, 7.36: nitrobenzene, 16.20%.

Tri(5-bromosalicylaldehyde)-diimine-iron(III) + Bromobenzene.—The black brown powder obtained above is recrystallized from bromobenzene. Dark violet needles.

Found: N, 3.64; Fe, 6.90; drying loss, 19.81. Calcd. for $C_{21}H_{12}N_2O_3Br_3Fe\cdot C_6H_5Br$: N, 3.54; Fe, 7.05; bromobenzene, 19.81%.

Tri(5-chlorosalicylaldehyde)-diimine-iron(III) + Nitrobenzene.—The reddish brown powder is obtained by the same treatment as in the case of the bromoderivative, using a solution of 5, 5′, 5″-trichlorohydrosalicylamide (3.5 g.) (or 5-chlorosalicylaldehyde and ammonia) in alcohol (60 cc.) and a solution of ammonium ferric sulfate (dodecahydrate; 4 g.) in water (20 cc.). Yield 3 g. This powder is recrystallized from nitrobenzene. Black plates.

Found: N, 6.88; Fe, 9.05; drying loss, 19.49. Calcd. for $C_{21}H_{12}N_2O_3Cl_3Fe\cdot C_6H_5NO_2$: N, 6.72; Fe, 8.93; nitrobenzene, 19.67%.

Tri(5-chlorosalicylaldehyde)-diimine-iron(III) + Bromobenzene.—This is prepared by the recrystallization of the powder from bromobenzene. Dark violet needles.

Found: N, 4.01; Fe, 8.64; drying loss, 23.55. Calcd. for $C_{21}H_{12}N_2O_3Cl_3Fe\cdot C_6H_5Br$: N, 4.24; Fe, 8.47; bromobenzene, 23.80%.

Tri(5-nitrosalicylaldehyde)-diimine-iron(III) + Nitrobenzene.—A Solution of 5, 5′, 5″-trinitrohydrosalicylamide (1 g.) in alcohol (50 cc.) is warmed on a water bath and a solution of ammonium ferric sulfate (dodecahydrate: 0.7 g.) in water (10 cc.) is added to it. The resulting reddish brown precipitates are treated as before. This powder is insoluble in common organic solvents and slightly soluble in nitrobenzene. When the powder is recrystallized from nitrobenzene, a small amount of crystals is obtained after about two days.

Found: N, 12.41; Fe, 8.43; drying loss, 18.48. Calcd. for $C_{21}H_{12}N_5O_9Fe\cdot C_6H_5NO_2$: N, 12.79; Fe, 8.50; nitrobenzene, 18.70%.

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