

metric titrations. Terpyridine is too insoluble in water and too weak a base to permit its direct titration in this medium. The titrations were made using various solvents (glacial acetic acid, chlorobenzene, dioxane). Perchloric acid in glacial acetic acid was used as the titrant.

When titrated in this manner, terpyridine gave only one inflection point on the potentiometric curve in each solvent. This point occurred at a volume of titrant corresponding to exactly two equivalents of acid per mole of terpyridine. If terpyridine were taking up two protons per mole, two inflection points might be expected in the potentiometric curves. Since double inflection points were not obtained, a series of conductometric titrations were also carried out using the same solvents. Here, as in the potentiometric series, only one inflection point was obtained in each case at a volume of titrant corresponding to exactly two equivalents of acid per mole of terpyridine.

Determination of the Acid Dissociation Constant.—The acid dissociation constant for terpyridine was determined by sodium hydroxide titration of weighed samples of terpyridine dissolved in a hydrochloric acid solution containing an amount of acid exactly equivalent to the amount of terpyridine. Only one inflection point was observed.

The half-way point on the potentiometric curve obtained was taken as a measure of the geometric average value for the two acid dissociation constants involved. On this basis, the composite pK_a is 7.1.

Determination of the Instability Constant.—Solutions were prepared containing varying amounts of iron(II) and sulfuric acid. The equilibrium concentration of the complex was determined spectrophotometrically at 550 $m\mu$. From the data, the equilibrium constant for the reaction of the bis-terpyridine-ferrous complex with hydrogen ion was calculated. The values from nine experiments varied from $1.3-3.4 \times 10^{-4}$. The average instability constant for the complex calculated from these values and the acid dissociation constant was 1×10^{-13} .

Discussion

A direct comparison of the instability constants of the ferrous complexes of 1,10-phenanthroline, 2,2'-bipyridine and 2,2',2''-terpyridine is prevented by the difference in the number of organic molecules and the number of hydrogen ions involved. These differences may be resolved by calculating an "average basicity" for each nitrogen atom involved in the chelation. This then permits a comparison similar to the correlation of instability constant and basicity of the organic molecules which has been previously demonstrated for a series of substituted 1,10-phenanthroline complexes.⁵ Table I contains the known instability constants and

TABLE I
AVERAGE NITROGEN BASICITIES

Compound	pK_a	Nitrogen atoms per molecule	Av. basicity per nitrogen atom	pK_D
2,2',2''-Terpyridine	7.10	3	2.37	18.0
2,2'-Bipyridine ^a	4.35	2	2.18	17.3
1,10-Phenanthroline ^b	4.95	2	2.48	21.3
5-Methyl-1,10-phenanthroline ^b	5.23	2	2.62	22.3
5-Chloro-1,10-phenanthroline ^b	4.26	2	2.13	19.7
5-Nitro-1,10-phenanthroline ^b	3.57	2	1.79	17.8

^a A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice-Hall, Inc., New York, N.Y., 1952. ^b Reference 5.

the calculated "average basicities." The graphical relationship is shown in Fig. 1. The position of bipyridine demonstrates the erroneous nature of a previous report.⁵ The similarity between the

(5) W. W. Brandt and D. K. Gullstrom, *THIS JOURNAL*, **74**, 3532 (1952).

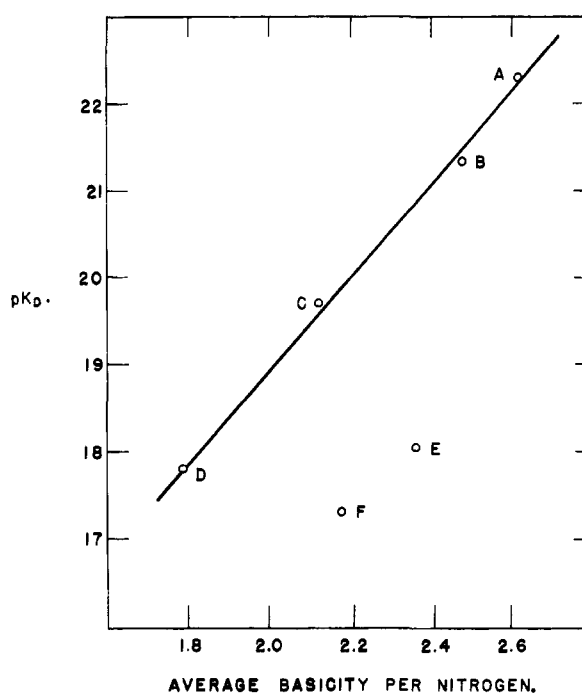


Fig. 1.—A comparison of the stabilities of several chelate complexes of iron(II): A, 5-methyl-1,10-phenanthroline; B, 1,10-phenanthroline; C, 5-chloro-1,10-phenanthroline; D, 5-nitro-1,10-phenanthroline; E, 2,2',2''-terpyridine; F, 2,2'-bipyridine.

juxtaposition of the bipyridine and terpyridine values indicates that it may be due to the dissimilarity of their ring systems from that of 1,10-phenanthroline.

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Diffraction of X-Rays by the Ferric Chloride-Aniline Complex

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Previous preparations²⁻⁵ of the ferric chloride-aniline complexes have involved acid reactions in aqueous solutions and no X-ray diffraction data have been reported. In order to form the reaction products characteristic of the bulk reaction of anhydrous ferric chloride and dry aniline, the complexes were made by the following methods.

(1) Addition of a 50% aniline in dry benzene solution to a solution of 0.56 g. per 100 ml. of anhydrous ferric chloride in dry benzene in the molar ratios of one to one, six to one, and twelve to one.

(2) Addition of aniline to a solution of 17% ferric

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(2) J. L. C. Schoreder van der Kolk, *Z. anal. Chem.*, **35**, 301 (1896).

(3) R. M. McKenzie, *Am. Chem. J.*, **50**, 308 (1913).

(4) Y. Osaka, G. Shima and R. Yoshida, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **7**, 69 (1924).

(5) J. V. Dubsy and E. Wagenhofer, *Z. anorg. allgem. Chem.*, **230**, 112 (1936).

chloride in absolute ethyl alcohol in the molar ratios of two to one and four to one.

(3) Exposure of anhydrous ferric chloride crystals to aniline vapor in a desiccator, in the presence of P_2O_5 .

Anhydrous ferric chloride was obtained in 1-oz. bottles from Eimer and Amend Co. and freshly opened for each solution. Solution concentrations were obtained by chloride analysis. Samples precipitated in benzene or made from the vapor reaction were subjected to X-ray diffraction without recrystallization. Samples precipitated from alcohol were recrystallized from 95% benzene-5% absolute alcohol solvent.

The X-ray diffraction photographs were taken with CuK_{α} radiation using a nickel foil filter and a 14.32-cm. diameter camera. Two distinct crystalline patterns appeared from the samples. The complex formed from the aniline vapor and ferric chloride and from the one to one molar ratio in benzene had the following pattern.

d	I/I_0	d	I/I_0	d	I/I_0
11.27	0.07	2.14	0.67	1.64	.35
5.53	.86	2.05	.20	1.53	.45
4.40	.25	1.99	.14	1.48	.15
4.05	.54	1.96	.04	1.39	.17
3.52	.25	1.88	.17	1.37	.31
3.03	.96	1.83	.32	1.28	.12
2.79	.37	1.80	.36	1.24	.04
2.21	1.00	1.74	.27		

d = interplanar spacing measured in ångstrom units

I = intensity of the diffraction line (arbitrary units)

I_0 = intensity of the strongest line

The complex precipitated by the reaction of two and four moles of aniline to one of ferric chloride in alcohol, and six and twelve moles of aniline to one of ferric chloride in benzene had the following pattern.

d	I/I_0	d	I/I_0	d	I/I_0
11.27	1.00	3.90	0.57	2.29	0.58
10.32	.98	3.70	.38	2.14	.25
8.63	.98	3.52	.38	2.05	.38
7.70	.52	3.34	.49	1.96	.45
6.66	.36	3.15	.50	1.88	.45
5.65	.43	3.03	.61	1.83	.32
5.25	.54	2.89	.42	1.76	.25
4.99	.36	2.79	.18	1.72	.14
4.78	.34	2.70	.50	1.64	.33
4.40	.66	2.59	.32	1.61	.33
4.05	.30	2.53	.78		

Relative intensities were taken from densitometer tracings of the film, treated according to the method described by Gardner, Cohen and Antia.⁶ The relative intensities vary to some extent for different preparations. However, the specimens were packed on a wedge holder without standardization of dimensions or shape beyond the limits imposed by packing the specimen in place. The intensities given were taken from the photographs of the aniline vapor reaction and of the precipitate from the one to six molar ratio in benzene.

The line of the 11.27 Å. plane was just barely visible in the first pattern ($I/I_0 = 0.07$) and may have been due to traces of the second complex where $I/I_0 = 1.00$ for the 11.27 plane. Lines representing the 10.32 and 8.63 Å. planes of the second pattern ($I/I_0 = 0.98$) were not visible on the first pattern, but corresponded to small rises in the densitometer tracings. The lines of 1.00 and 0.86 relative intensity of the first pattern were missing in the second pattern, although some of the less intense lines are common to both. In comparing the patterns given

(6) F. S. Gardner, M. Cohen and D. P. Antia, *Metals Technol.*, **10**, T. P. 1560 (Feb. 1943).

here with spacings listed for anhydrous $FeCl_3$,⁷ it is found that the 5.9 Å. spacing ($I/I_0 = 0.32$) of $FeCl_3$ is missing in both patterns, while the 2.68 Å. ($I/I_0 = 1.00$) and 5.7 Å. ($I/I_0 = 0.32$) spacings are missing in the first pattern. Some of the other spacings are close enough to possibly coincide, but a number of the more intense lines of the ferric chloride-aniline complexes are not listed, or are of very low intensity, for $FeCl_3$.

Iron analysis, by reduction with $SnCl_2$ and oxidation with dichromate showed 21.8% Fe for the sample from a one to one molar ratio solution in benzene and 16.3 and 17.0% Fe for the samples from six to one and twelve to one ratios of aniline to ferric chloride in benzene. The theoretical amount of iron in a one to one molar ratio compound would be 21.9% and in a two to one molar ratio compound 16.7%. The absence of solvent of crystallization in the samples was indicated by the identity of diffraction patterns for the first compound formed both with and without solvent and by the identity of the diffraction patterns of the second compound made from both alcohol and benzene solutions. The results indicate that the molar ratios one to one and two to one of aniline to ferric chloride were the compounds formed and there was no evidence of any higher ratios comparable to the acid hexa-anilinium salts reported by previous investigators.²⁻⁴

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(7) J. O. Hanawalt, H. W. Rinn and L. V. Frevel, *Ind. Eng. Chem., Anal. Ed.*, **10**, 510 (1938).

The Specific Heats of Concentrated Sodium and Potassium Bromide Solutions at 25 and 30°

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The range of concentration covered in the specific heat measurements on dilute sodium and potassium bromide solutions made by Randall and Rossini¹ extended to the one molal level. Results are here reported for higher concentrations.

Experimental Details

Calorimeter.—An isothermal-jacket calorimeter of essentially conventional design was employed. The calorimeter vessel, which held about 730 ml. of solution, was made of brass and heavily silver plated; it was supported, on three Micalox cones, in a submarine jacket in an oil thermostat controlled by a mercury thermoregulator.

The calorimeter heater was made from enameled constantan wire, wound over thin mica insulation on a brass spool and covered with a close-fitting brass sleeve which was soldered in place. One end of the coil was connected directly to the brass shell; the other lead was taken out of the housing through a Kovar hermetic seal, and thence out of the calorimeter vessel through a brass tube which was one of the supports holding the heater assembly to the vessel cover. The calorimeter stirrer operated inside the cylindrical heater unit. The calibrations of the standard cell, standard resistance and voltage divider used in the electrical measurements were checked by the Electrical Standards Laboratory

(1) M. Randall and F. D. Rossini, *This Journal*, **51**, 323 (1929).