to a solution of 1.10 g. of zirconium isopropoxide (0.00284 mole) in benzene (40 g.) gave a white shining crystalline precipitate on shaking. After being left overnight for complete crystallization, the compound was filtered, washed with benzene (15 cc.) and dried under reduced pressure (2 mm.) at room temperature.

Anal. Calcd. for $Zr(OOC{\cdot}C_6H_5)_4$: Zr, 15.86; $(OOC{\cdot}C_6H_5)$, 84.14. Found: Zr, 15.62; $(OOC{\cdot}C_6H_5)$, 84.3.

Reaction of Zirconium Isopropoxide with Excess Phenol.—A solution of 2.07 g. of zirconium isopropoxide (0.0053 mole) dissolved in benzene (66 g.) and 4.0 g. of phenol (0.0426 mole) gave a clear solution on shaking. The mixture was refluxed in a bath at 110°. The amount of isopropyl alcohol in the distillate collected in 2 hr. (about 30 ml.) was 1.52 g. (0.0253 mole). Pure benzene was distilled out under a high reflux ratio. The clear solution was left overnight for crystallization. A white shining mass crystallized out. The crystals were filtered, washed with benzene and then dried as usual.

Anal. Calcd. for $Zr{\cdot}(C_6H_5O)_4{\cdot}C_6H_5OH$: Zr, 16.25; (OC_6H_5), 83.75. Found: Zr, 16.3; (OC_6H_5), 82.06.

Reaction between Zirconium Isopropoxide with Excess Benzoic Acid and Phenol.—To a solution of 1.88 g. of phenol (0.0200 mole) and 2.44 g. of benzoic acid (0.0195 mole) in benzene (69 g.) was added 1.59 g. of zirconium isopropoxide (0.0041 mole), and a clear solution was obtained. The mixture was refluxed in a bath at 110°. The amount of isopropyl alcohol in the distillate (about 30 ml.) was 1.20 g. (0.0200 mole). Remaining benzene was distilled out under a high reflux ratio. The reaction mixture was left for crystallization, when a white mass crystallized out. The crystals were filtered, washed with dry benzene and dried in the usual manner.

Anal. Calcd. for $Zr(OOC{\cdot}C_6H_5)_4$: Zr, 15.86; $(OOC{\cdot}C_6H_5)$, 84.14. Found: Zr, 18.01; $(OOC{\cdot}C_6H_5)$, 81.48.

Reaction between Zirconium Tetrachloride and Salicylic Acid in Benzene.—The addition of 1.86 g. of salicylic acid (0.0135 mole) to a suspension of 0.7 g. of zirconium tetrachloride (0.00303 mole) in benzene (28 g.) gave a white precipitate on shaking. The reaction mixture was refluxed in a bath at 110° for nearly 24 hr. till the evolution of hydrogen chloride gas almost ceased. The product was filtered, washed with dry benzene and dried under reduced pressure (2 mm.) in a bath at 40° for nearly 2 hr.

Anal. Calcd. for $(OOC{\cdot}C_6H_4O)Zr\ (OOC{\cdot}C_6H_4OH)_2$: Zr, 18.18; (HOC_6H_4COO), 81.99. Found: Zr, 18.28; (HOC_6H_4COO), 81.28.

Reaction between Zirconium *Iso*propoxide and Excess Methyl Salicylate in Benzene.—To a solution of 1.50 g. of zirconium *iso*propoxide (0.0038 mole) in benzene (60 g.) was added 2.93 g. of methyl salicylate (0.0193 mole), when a clear solution was obtained. The mixture was refluxed in a bath at 110°. About 40 ml. of the distillate were collected slowly between 71–80° in the course of about 3 hr. The remaining benzene was removed under a high reflux ratio and the reaction mixture (15 ml.) was left for crystallization. A shining white crystalline mass separated out. After decantation, the product was recrystallized from benzene (10 ml.). Now the crystals were separated by decantation and dried under reduced pressure (2 mm.) at a bath (50°) for nearly 2 hr. The solid has a sharp melting point of 187°.

Anal. Calcd. for $Zr{\cdot}(OC_6H_4CO_2CH_3)_4$: Zr, 13.11. Found: Zr, 12.93.

Acknowledgments.—The authors are grateful to the Council of Scientific and Industrial Research for a research grant and assistantship awarded to one of them (R.N.K.). Thanks are due to Magnesium Electron Ltd., London, for zirconium tetrachloride.

[CONTRIBUTION NO. 1575 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, NEW HAVEN, CONNECTICUT]

The Detection of a Type of Reaction Intermediate in the Combination of Metal Ions with Porphyrins

BY EVERLY B. FLEISCHER[1] AND JUI H. WANG

RECEIVED DECEMBER 7, 1959

A reaction intermediate in the combination of metal ions with porphyrins is detected and studied. A structure with the metal sitting-atop the flat porphyrin molecule is proposed for this intermediate compound. Spectroscopic and equilibrium data of these sitting-atop type of complexes are presented.

The metalloporphyrins, which are known to be very stable metal complexes, have been extensively studied both experimentally[2] and theoretically.[3] It has been demonstrated[4] that many metal ions in the porphyrin complex, such as Fe(II), Fe(III), Co(III), Ni(II), etc., do not undergo detectable exchange with similar ions in solution. In order to extract these transition metal ions from the metalloporphyrins, it is necessary to use concentrated hydrochloric or even sulfuric acid at high temperature. Conversely, even in basic aqueous solutions it is often necessary to heat the reaction mixture in order to introduce a transition metal ion into the porphyrin ring.[2] Based on their kinetic studies, Phillips and co-workers[5] suggested that the reaction between zinc ion and solubilized porphyrin esters to form the corresponding metalloporphyrin takes place, as indicated in the reaction below, through a displacement rather than a dissociation type of mechanism.[6]

$$Zn^{++} + RH_2 + 2H_2O \rightleftharpoons RZn + 2H_3O^+$$

where RH_2 represents the porphyrin. We want to report some results which show not only that the reaction between metal ion and porphyrin to form metalloporphyrin takes place through a displacement mechanism but also that the metal ion first combines with the porphyrin to form a reaction intermediate which subsequently decomposes to the normal metalloporphyrin and two hydrogen ions. Our work shows that this reaction intermediate has a structure depicted in Fig. 1, with the metal ion sitting atop the flat porphyrin molecule. The

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[1] National Science Foundation Predoctoral Fellow, 1959–1960.

[2] For general references, see R. Lemberg and J. W. Legge, Hematin Compounds and Bile Pigments, Interscience Publishers, Inc., New York, 1949.

[3] *Discussions Faraday Soc.*, **No. 26**, 81 (1958).

[4] S. Ruben, M. Kamen, B. Allen and P. Nahinsky, THIS JOURNAL, **64**, 2297 (1942).

[5] B. Dempsey, M. B. Lowe and J. N. Phillips, paper presented at the Symposium on Hematin Enzymes, Canberra, Australia, Aug. 31–Sept. 4, 1959.

[6] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 91.

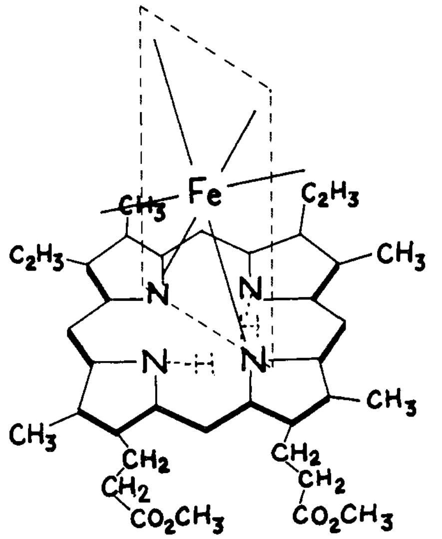
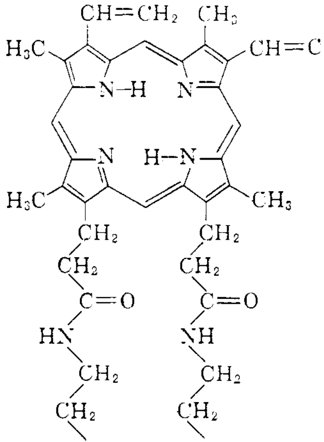


Fig. 1.—Proposed sitting-atop type of structure for the reaction intermediate.

evidences for the existence of this sitting-atop type of complex are summarized in the following.

Visible Spectra.—The spectra of protoporphyrin and its complexes are shown in Fig. 2. If equivalent amounts of Fe(III)-salt and the water-soluble protoporphyrin derivative I are mixed in aqueous solution at room temperature, the visible spectrum of the mixture is essentially the same as that of I which is almost indistinguishable from that of the dimethyl ester of protoporphyrin shown in Fig. 2A. Upon prolonged heating above 50°, the spectrum of the mixture gradually changes to that of a hematin derivative as that illustrated in Fig. 2B. Spectroscopically no intermediate compound was detected in this process. We found that the rates of the successive steps in this reaction could be affected markedly by varying the solvent composition, presumably due to the change in solvation of the ions. For example, in acetone solutions some metal ions, Ni(II), Cu(II), Bi(III), Hg(II), Cd(II) react readily with dimethyl ester of protoporphyrin even at room temperature to form the corresponding metalloporphyrins, whereas other metal ions, Fe(II), Fe(III), Co(II), Pt(IV), Sn(II), Zn(II), etc., first form a new type of complex, with absorption spectra markedly different from that of the metalloporphyrins, which upon prolonged standing at 60° change to the corresponding metalloporphyrins.



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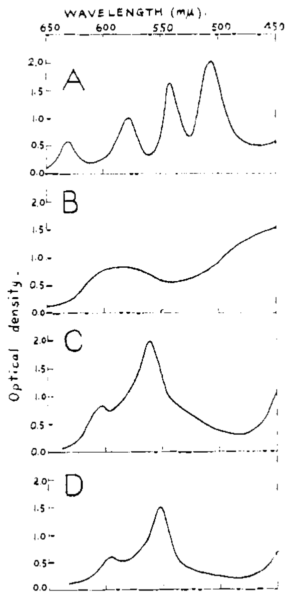

Fig. 2.—Visible spectra of protoporphyrin derivatives: (A) protoporphyrin dimethyl ester; (B) hemin dimethyl ester; (C) Fe(III)-SAPP; (D) dihydrochloride of protoporphyrin dimethyl ester.

Fig. 2C shows the visible spectrum of such a complex formed by treating ferric chloride with the dimethyl ester of protoporphyrin in chloroform solution. If alcohol or pyridine is added to this chloroform solution, the spectrum changes immediately back to that of protoporphyrin, 2A. This shows that the binding between Fe(III) and protoporphyrin in the new complex is quite weak, as the protoporphyrin readily can be displaced by other ligands. We suggest that this new complex has a sitting-atop type of structure illustrated in Fig. 1. It is also of interest to note that the spectrum of the sitting-atop complex Fe(III)–protoporphyrin dimethyl ester (hereafter referred to as Fe(III)–SAPP) bears a striking resemblance to that of protoporphyrin diacid, RH_4^{++}, as shown in Fig. 2D. This observation suggests that the observed absorption is probably due to electronic transitions in the protoporphyrin rather than the metal ion part of the complex. Similarly if the acetone solutions of the sitting-atop complexes of Fe(II), Fe(III), Co(II), Pt(IV), Zn(II), respectively, are diluted with water, the spectra immediately change to that of the dimethyl ester of protoporphyrin itself, Fig. 1A, as water molecules rapidly displace the organic ligand in the complex.

The visible spectra of the sitting-atop complexes of a number of transition-element ions are summarized in Table I. The visible spectrum of protoporphyrin diacid, RH_4^{++}, shows two absorption maxima at 553 and 596 mμ, respectively. It is also of interest to note that the spectra of uranyl and vanadyl complexes are quite similar to the others, although the structures of uranyl and vanadyl ions are quite different from those of the other ions.

Infrared Spectra.—The infrared spectra of protoporphyrin and Fe(III)–protoporphyrin complexes are shown in Fig. 3.

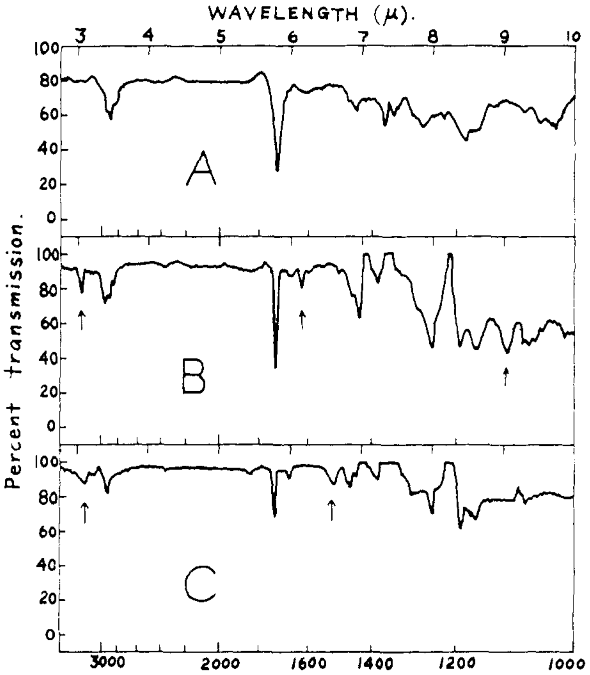

Fig. 3.—Infrared spectra of protoporphyrin derivatives: (A) hematin dimethyl ester; (B) protoporphyrin dimethyl ester; (C) Fe(III)–SAPP.

Several absorption peaks in the infrared spectrum of protoporphyrin dimethyl ester, Fig. 3B, have been assigned to vibrational modes of the N–H group.[7,8] In protoporphyrin dimethyl ester, Fig. 3B, the 3.05μ peak is due to the N–H stretching vibration, the 6.15μ peak due to N–H deformation and the 9.06μ peak due to the N–H rocking vibration. When the two N–H groups were changed to N–D groups by isotopic-exchange with deuterium oxide, the 3.05μ peak shifted to 4.17μ. If one compares the spectrum of Fig. 3B with the infrared spectrum of hemin dimethyl ester, Fig. 3A, one observes that all the above N–H peaks disappear as expected. The infrared spectrum of Fe(III)–SAPP, Fig. 3C, shows that the vibrational frequencies 3.05 and 6.15μ are shifted to 3.11 and 6.64 μ, respectively, and that the 9.06μ peak in 3B apparently disappeared in the spectra of Fe(III)–SAPP. This 9.06 μ peak has been assigned to a bending vibration similar to a wagging type except that the groups swing as a unit back and forth in the symmetry plane of the molecule.[8] The observed frequency shift of the 3.05 and 6.15μ peaks is due to the polarizing influence of the Fe-(III) on the N-atoms to which the former is bound.

Table I

Visible Spectra of Some Sitting-atop Complexes of Transition Element Ions with Protoporphyrin Dimethyl Ester in Acetone Solution

Metal ion	Wave lengths of observed absorption maxima (mμ)			
Fe(II)	536	568[a]	610	
Fe(III)		560[a]	603	
Cr(III)	538	562[a]	605	
Pt(IV)		563[a]	602	644
Sn(II)		561[a]	600	641
Zn(II)	538	563[a]	600	645
V(IV)[b]		558[a]	600	
U(VI)[c]	536	567[a]	600	

[a] Main absorption peak. [b] Vanadyl salt. [c] Uranyl salt.

Composition of the Fe–SAPP Complex.—The composition of the complex Fe–SAPP was determined by Job's method of continuous variations[9] as follows. In order to study the reaction

$$A + nB \rightleftarrows AB_n$$

solutions of varying stoichiometric mole-fraction, X, of B, but of constant total stoichiometric concentration, M, of A and B, were prepared. If C_1, C_2 and C_3 represent the concentrations of A, B, and AB_n, respectively, in the equilibrium mixture, we have

$$C_1 + C_3 = M(1 - X) \qquad (1)$$

$$C_2 + nC_3 = MX \qquad (2)$$

$$C_1C_2^n = KC_3 \qquad (3)$$

If we impose the condition that $\frac{dC_3}{dX} = 0$, then equations 1, 2 and 3 can be combined to give

$$n = \frac{X}{1 - X} \qquad (4)$$

The value of X can be determined experimentally by plotting a quantity Y which is proportional to C_3 *vs.* the stoichiometric mole-fraction X and taking the point where Y is either a maximum or minimum. In the present work the quantity Y used as a measure of C_3 is defined as

$$Y = D - D_0$$

where D is the optical density of the equilibrium mixture, and D_0 is the optical density the solution would have if no complex were formed. D_0 can be computed from the experimentally determined molar extinction coefficients of ferric chloride and protoporphyrin dimethyl ester, respectively, in chloroform solutions. Since the molar extinction coefficients of ferric chloride at the wave length used in the present work, 506 and 568 mμ, are very much smaller than that of protoporphyrin dimethyl ester, ϵ_{PP}, and that of the complex, $\epsilon_{complex}$ it can be shown that Y has a maximum value if $\epsilon_{complex} > \epsilon_{PP}$, or a minimum value if $\epsilon_{complex} < \epsilon_{PP}$. Figure 4 shows the plot of Y *vs.* X for solutions of protoporphyrin dimethyl ester and ferric chloride in chloroform. Fig. 4(a), at 568 mμ where $\epsilon_{complex} > \epsilon_{PP}$, shows a maximum at $X = 0.5$; Fig. 4(b), at 506 mμ where $\epsilon_{complex} < \epsilon_{PP}$, exhibits a minimum at $X = 0.5$. Thus n, in equation 4, is equal to unity, which shows that the molar ratio of Fe(III) to PP in the complex is 1:1.

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(7) C. S. Vestling and J. R. Downing, This Journal, **61**, 3511 (1939).

(8) H. M. Randall, R. G Fowler, N. Fuson and J. R. Dangl, "Infrared Determinations of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, pp. 45, 57.

(9) W. C. Vosburgh and G. P. Cooper, This Journal, **63**, 437 (1941).

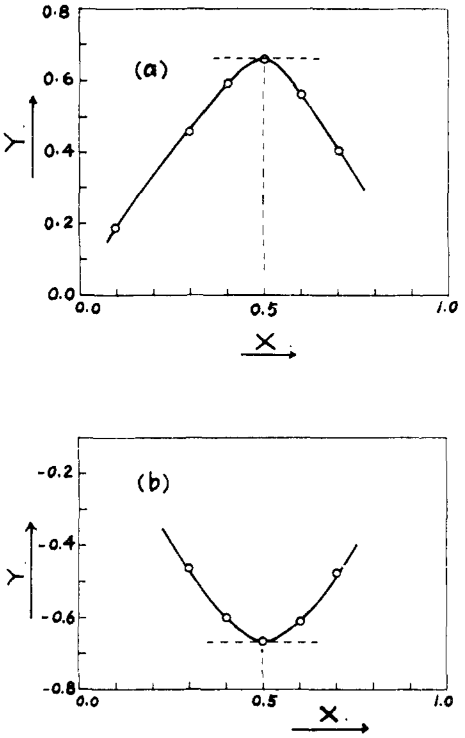

Fig. 4.—Graphical determination of *n*.

Equilibrium Studies.—Since it was known that ferric chloride exists in dimeric form[10] Fe_2Cl_6, when dissolved in poorly coördinating solvents like chloroform, equilibrium measurements were carried out to determine if the Fe(III)–SAPP complex also exists as a dimer in solution. The formation constant of Fe(III)–SAPP was so large in pure chloroform solution that it was necessary to add some ethanol to the system to reduce the formation constant somewhat for convenient equilibrium measurements. These four equilibria may exist in the mixture:

$$FeCl_3 + PP \rightleftarrows FeCl_3\text{–SAPP},\ K_1 = \frac{[FeCl_3\text{–SAPP}]}{[FeCl_3][PP]} \quad (I)$$

$$Fe_2Cl_6 + 2PP \rightleftarrows 2FeCl_3\text{–SAPP},\ K_{II} = \frac{[FeCl_3\text{–SAPP}]^2}{[Fe_2Cl_6][PP]^2} \quad (II)$$

$$2FeCl_3 + 2PP \rightleftarrows Fe_2Cl_6\text{–SA}(PP)_2,\ K_{III} = \frac{[Fe_2Cl_6\text{–SA}(PP)_2]}{[FeCl_3]^2[PP]^2} \quad (III)$$

$$Fe_2Cl_6 + 2PP \rightleftarrows Fe_2Cl_6\text{–SA}(PP)_2,\ K_4 = \frac{[Fe_2Cl_6\text{–SA}(PP)_2]}{[Fe_2Cl_6][PP]^2} \quad (IV)$$

For simplicity, the participation of ethanol molecules in the above reactions is omitted.

The concentrations of various species in the equilibrium mixture were determined by a spectrophotometric method. If D represents the optical density of an equilibrium mixture of PP, ferric chloride and the sitting-atop complex, and D_∞ represents that of a solution containing the same total amount of PP per cc. but all in the complex form, then $\frac{D_0 - D}{D_0 - D_\infty}$ is equal to the fraction of total PP in the complex form in the equilibrium mixture. Pure PP itself was found by our freezing point depression measurements to exist in monomeric form in bromoform, $CHBr_3$, solution. By analogy we may infer that pure PP also exists in monomeric form in chloroform solutions. Since the total stoichiometric concentrations of protoporphyrin dimethyl ester and ferric chloride are known, the concentrations of all the individual species in the equilibrium mixture can be calculated.

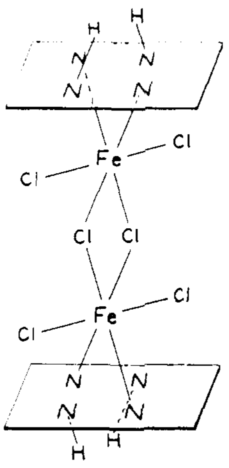

Fig. 5.—Proposed dimeric structure of the sitting-atop type of complex.

Table II summarizes the result of measurements in chloroform solutions containing 2.5% by volume of methanol. Of the four equilibrium constants defined above, it is seen that only K_I, which is equal to $3.9 \pm 0.2\ M^{-1}$, remains essentially constant for solutions of varying concentrations of the reactants. This shows that in 2.5% by volume of methanol in chloroform solution, ferric chloride is in monomeric form and reacts with PP to form $FeCl_3$–SAPP. Presumably in this complex the Fe(III)-ion is octahedrally coördinated to two of the N-atoms of PP, three chloride ions and a methanol molecule. Measurements also were made in chloroform solutions containing 3.0% by volume of methanol. In these solutions K_I still remains essentially constant but has a smaller value, $2.0 \pm 0.2\ M^{-1}$.

TABLE II

EQUILIBRIUM MEASUREMENTS IN CHLOROFORM SOLUTIONS CONTAINING 2.5% BY VOLUME OF METHANOL

[Sitting-atop complex] (mM)	[Free PP] (mM)	[Free $FeCl_3$] (mM)	$K_I \times 10^{-3}$	$K_{II} \times 10^{-3}$	$K_{III} \times 10^{-9}$	$K_{IV} \times 10^{-6}$
2.95	8.95	0.87	3.79	2.54	24.3	4.25
3.72	8.18	1.05	4.33	3.94	25.1	5.27
4.33	7.57	1.40	4.07	4.58	18.0	5.30
4.89	7.01	1.79	3.91	5.46	15.6	5.57
5.47	6.43	2.17	3.92	4.68	14.1	6.10
6.35	5.55	3.20	3.60	8.24	10.1	6.50

The results in 1.0% by volume methanol in chloroform solutions are summarized in Table III. Here it is seen that K_I no longer remains constant, but K_{IV} seems to approach a fairly constant value

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[10] For references to the literature, see N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. II, Oxford Univ. Press, 1950, p. 1355.

over the range of concentrations studied. This indicates that as we reduce the methanol concentration, the equilibrium gradually shifts from I to IV and that in pure chloroform solution the sitting-atop complex probably exists in the form of a dimer, Fe_2Cl_6–SA$(PP)_2$. A probable structure of this dimeric complex is depicted in Fig. 5.

TABLE III

EQUILIBRIUM MEASUREMENTS IN CHLOROFORM SOLUTIONS CONTAINING 1.0% BY VOLUME OF METHANOL

[Sitting-atop complex] (mM)	[Free PP] (mM)	[Free $FeCl_3$] (mM)	$K_{I} \times 10^{-3}$	$K_{IV} \times 10^{-6}$
5.36	3.41	0.37	42.5	125
6.62	2.15	1.02	30.0	139
7.30	1.34	2.12	26.1	150

On the other hand if more than 10% by volume of methanol is added to the chloroform solution, the PP in Fe(III)–SAPP is completely displaced by methanol molecules, and the sitting-atop complex can no longer exist in solution as shown by the visible spectra.

Experimental

The dimethyl ester of protoporphyrin was prepared by the method of Grinstein,[11] with the exception that recrystallized samples of hemin, supplied by Fisher Scientific Company, recrystallized (97 + %), were used instead of fresh blood as the raw material. The m.p. of the dimethyl ester of protoporphyrin so prepared is 221°. The anhydrous ferric chloride has a m.p. of 282°.

All visible spectra were taken on a Cary Recording Spectrophotometer. The infrared spectra were taken with a Perkin–Elmer Recording Infrared Spectrophotometer with a matched pair of 0.1 mm. sodium chloride cells. Deuterated chloroform, 99% $CDCl_3$, was used as solvent to dissolve the Fe(III)–SAPP for infrared studies. All the measurement were made at room temperatures of 20 to 23°.

The N,N′-bis-(2-aminoethyl) diamide I was prepared by dissolving the dimethyl ester of protoporphyrin in excess of ethylenediamine and heating the mixture at 100° for several hours under nitrogen atmosphere in a sealed tube. The excess ethylenediamine was removed by vacuum evaporation. The purified product I was completely soluble in water.

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(11) M. Grinstein, *J. Biol. Chem.*, **167**, 515 (1947).

[CONTRIBUTION FROM THE ELECTRON TUBE DIVISION, RADIO CORPORATION OF AMERICA, LANCASTER, PENNSYLVANIA]

Preparation of the Compound $7MgO{\cdot}2SnO_2{\cdot}As_2O_5$

BY ARTHUR L. SMITH

RECEIVED DECEMBER 9, 1959

Analysis of a portion of the system $MgO–SnO_2–As_2O_5$ by means of X-ray diffraction discloses the existence of the compound $7MgO{\cdot}2SnO_2{\cdot}As_2O_5$. The compound may be prepared by heating the respective oxides in requisite proportion at 1200° for 4 hr. The characteristic X-ray diffraction pattern of the compound is given.

Introduction

Compounds containing all three type oxides, MO, MO_2 and M_2O_5, are relatively rare. The present compound was discovered during an investigation to improve the luminescence of the phosphor $6MgO{\cdot}As_2O_5$:Mn by coactivation with tin(IV) oxide. Anomalies in the luminescence data prompted a study of the ternary system. Because the $MgO + SnO_2$ and $MgO + As_2O_5$ edges have been defined through the work of previous investigators, only that portion of the ternary which was necessary to identify the new compound was studied.

The work of Tanaka,[1] Berezhnov,[2] Coffeen[3] and Coughanour, *et al.*,[4] on the magnesium oxide–tin(IV) oxide solid-state reaction may be summarized as follows: Two compounds exist, $2MgO{\cdot}SnO_2$ and $MgO{\cdot}SnO_2$. There is complete agreement that the compound $2MgO{\cdot}SnO_2$ is thermally stable to at least 1550°. Although Coffeen claimed thermal stability of the compound $MgO{\cdot}SnO_2$ above 1000°, Coughanour, in agreement with Tanaka, found it to be unstable in the region 800–1000°, decomposing to $2MgO{\cdot}SnO_2$ and SnO_2. The present work, all conducted in this system at 1000° or above, failed to detect the presence of $MgO{\cdot}SnO_2$. This further confirms the work of Coughanour and Tanaka.

The $MgO + As_2O_5$ reactions are more complicated than those of $MgO+SnO_2$ because of the volatility of arsenic pentoxide. Guerin[5] and Travnicek, *et al.*,[6] have noted the tendency of $MgO+As_2O_5$ compounds to lose $As_2O_3 + O_2$ during heating. Guerin states that $MgO{\cdot}As_2O_5$ loses arsenic oxide at 500° to give $2MgO{\cdot}As_2O_5$, which, in turn, loses arsenic oxide to form $3MgO{\cdot}As_2O_5$ at 900°. He also considered the orthoarsenate to be unstable but did not realize that its decomposition led to a new and definite compound. Travnicek, *et al.*, found that at temperatures above 1000° the loss of arsenic pentoxide from the orthoarsenate leads to the compound $6MgO{\cdot}As_2O_5$. This compound can be prepared directly by firing the requisite proportions of the oxides and is stable to at least 1250°. The present investigation supports Travnicek's findings, but the decomposition of the orthoarsenate has been found to be reasonably slow (about 10 to 20% decomposition at 1200° for 4 hr.).

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(1) Yasuo Tanaka, *J. Chem. Soc. Japan*, **61**, 1023 (1940); *Bull. Chem. Soc. Japan*, **16**, 428 (1941) (*C. A.*, **35**, 2776 (1941); *ibid.*, **41**, 4393 (1947).

(2) A. S. Berezhnov, *Compt. rend. acad. sci. U.R.S.S.*, **53**, 47 (1946), (*C. A.*, **41**, 1535 (1947).)

(3) W. W. Coffeen, *J. Am. Cer. Soc.*, **36**, 207 (1953).

(4) L. W. Coughanour, R. S. Roth, S. Marzullo and F. E. Sennett, *J. Research. Natl. Bur. Standards*, **54**, 149 (1955).

(5) Henri Guerin, *Compt. rend.*, **204**, 1740 (1937).

(6) M. Travnicek, F. Kroger, The P. J. Botden and P. Zalm, *Physica*, **18**, #1, 33 (1952).