diene polymers and copolymers and upon the vast difference in the rate at which vinyl and internal ethylenic bonds add mercaptans, it would appear that the 38 to 47% of ethylenic bonds which added mercaptans readily are probably those derived from 1,2-addition of butadiene units to the polymer chains, or those arising from 1,2-addition and intramolecular cyclization reactions.

The saturation values obtained by the reactions between various types of mercaptans and butadiene polymers are in fair agreement in spite of a wide range of reaction conditions.

If it is assumed that the polymer double bonds which added mercaptans readily are those present in side vinyl groups, then the mercaptan saturation values found are in fair agreement with the value of 48% for a butadiene–styrene copolymer as determined by potassium permanganate oxidation,[6] and 34.5 and 42.8% as determined by ozonolysis[3] for a butadiene–styrene and a sodium catalyzed polybutadiene, respectively. The mercaptan saturation values are not, however, in full agreement with those found by perbenzoic acid oxidation whereby emulsion butadiene–styrene copolymers showed 1,2-values of 27[6] and 20–22[7] per cent. while sodium catalyzed polybutadiene showed 58[7] per cent. side vinyl groups.

Summary

Thioglycolic acid added exothermally to butadiene polymers and copolymers in benzene solution under mild conditions to give apparent double bond saturation values of 38 to 47%. When the same polymers reacted with aliphatic mercaptans of C_2 to C_{16} chain length, in mass or latex reactions, saturation values were obtained which were in accord with those found by thioglycolic acid addition.

It is suggested that the double bonds in butadiene polymers and copolymers which were readily saturated by the above mercaptans are predominately those present in the polymer chains as vinyl side groups.

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[CONTRIBUTION FROM THE CHARLES F. KETTERING FOUNDATION FOR THE STUDY OF CHLOROPHYLL AND PHOTOSYNTHESIS, ANTIOCH COLLEGE, AND FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Porphyrin Studies. V.[1] The Metal Complex Salts of α,β,γ,δ-Tetraphenylporphine

BY PAUL ROTHEMUND AND AMEL R. MENOTTI[2,3]

In the preceding paper of this series[1] we reported the synthesis of α,β,γ,δ-tetraphenylporphine (hereafter to be abbreviated T.P.P.) on a preparative scale. Thus sufficient quantities of this porphyrin became available for the preparation and study of a large number of its metal complex salts, fifteen of which have been obtained in the present investigation in crystalline form and five in solution only.

This is probably the largest number of metal complex salts ever prepared from any one porphyrin, and the work was undertaken with the aim of furnishing reliable material for physico-chemical studies on the structure of porphyrin metal complexes, especially in connection with the study of chlorophyll. Spectrophotometric measurements on the above-mentioned series of compounds are in progress at the Charles F. Kettering Foundation in order to determine possible correlations between absorption and fluorescence spectra; some of the findings have already been published.[4]

The metal complex salts described are the derivatives of T.P.P. which shows the "etio type"[5] spectrum and has its first absorption band in ether solution at 648 mμ. Derivatives of isomers and of other polynuclear pyrrole pigments, by-products in the synthesis of T.P.P., will be described in a separate publication.

In the preparation of these metal complexes three general methods were employed which are described in detail in the experimental part.

General Properties of the Metal Complex Salts.—All of the salts isolated were well-crystallized compounds of high surface luster. They showed selective absorption in the visible region of the spectrum and had melting points ranging from 400 to 520°. On heating from 400 to 450° all but the manganese chloride and the gold salts sublimed. During this sublimation partial decomposition of the complex occurred.

The complexes varied markedly in stability. Thus, the potassium and one thallium complex decomposed when dissolved in neutral solvents such as benzene and ether; the magnesium, mercury, and lead complexes split when shaken with 50% acetic acid. The zinc and silver complexes were stable to 50% acetic acid but decomposed slowly in hydrochloric acid solutions. In every case of these decomposition conditions the presence of free porphyrin in the solution was ascertained. The iron chloride, manganese chloride, cobalt, nickel, copper, stannous chloride, and gold complexes were heated in the steam-bath with

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(1) Paper IV, THIS JOURNAL, **63**, 267 (1941).

(2) From the dissertation submitted by Amel R. Menotti to the Faculty of the Graduate School of the Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1940.

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(4) Knorr and Albers, *J. Chem. Phys.*, **9**, 197 (1941).

(5) Stern and Wenderlein, *Z. physik. Chem.*, **A170**, 348 (1934).

TABLE I

SOLUBILITY OF $\alpha,\beta,\gamma,\delta$-TETRAPHENYLPORPHINE METAL COMPLEX SALTS

VS = very soluble; S = soluble; SS = slightly soluble; VSS = very slightly soluble; I = insoluble; D = decomposes

	Mg	Zn	Cd	Hg	Cu	Ag	Sn	Pb	MnCl	FeCl	Co	Ni	Tl
Acetone	S	SS	SS	VSS	VSS	VSS	I	I	S	SS	I	I	I
Benzene	S	S	VS	SS	SS	S	SS	SS	S	S	S	SS	VSS
Chloroform	VS	VS	VS	VS	S	S	VS	S	VS	VS	S	S	VSS
Ether	S	S	S	VSS	SS	SS	I	I	S	VSS	SS	VSS	I
Ethyl acetate	S	SS	SS	I	SS	SS	I	VSS	S	SS	SS	I	I
Glacial acetic acid	D	VSS	D	D	VSS	I	I	D	S	VSS	SS	I	I
Methanol	I	VSS	VSS	I	I	I	I	I	VS	SS	I	I	I
Petroleum ether	I	I	I	I	I	I	I	I	SS	I	I	I	I
Pyridine	VS	VS	VS	VS	S	S	S	S	VS	VS	S	SS	VSS

concentrated hydrochloric acid for hours without any sign of decomposition.

The complexes of lithium, sodium, potassium, rubidium and cesium decomposed rapidly when their solutions were exposed to strong light; the magnesium and thallium (stabile compound) complexes showed spectrum shifts under these conditions. Solutions of the magnesium salt first showed a decrease in the intensity of the absorption band in the red and then decomposed to a solution without porphyrin spectrum on further exposure. The solubility data of the complex salts are given in Table I.

Upon heating of magnesium phthalocyanin with commercial tetralin Helberger[6] observed a new case of chemiluminescence, and demonstrated that a number of metal complex salts of different types of porphyrin pigments exhibit this luminescence reaction. Later Helberger and Hevér[7] studied the mechanism of the reaction in detail and ascertained that the presence of tetralin peroxide in commercial tetralin was responsible for the positive result; with other solvents these authors arrived at similar findings and rendered it highly probable that in every case impurities of peroxide types are present in the solvent. It is to be hoped that they will succeed in elucidating the conditions for this reaction, which may be of great interest in the field of photosynthesis research. From this point of view it seems desirable to test all new porphyrin metal complex salts under the conditions of Helberger's chemiluminescence reaction and give the results as additional characteristics of the compounds discussed. Of the complex salts described above, the magnesium, zinc, and cadmium salts were tested thus far. Each of them exhibited bright red chemiluminescence when heated above 125° in tetralin, xylene, *p*-cymene, or bromocyclohexane. When freshly distilled tetralin was employed, only a faint glow of short duration was obtained. On adding to the hot solution a few drops of tetralin which had been standing for some time, however, the bright red glow reappeared.

Experimental

General Remarks.—Three methods of preparation of the metal complex salts were used; they will be referred to in the following text by number, and only quantities of reagents and variants from the general procedure will be indicated specially.

Method 1 (Acid Medium).—The porphyrin solution in acetic (or formic) acid was heated under reflux with the acetate of the metal. In the preparation of the silver complex the di-silver salt was formed under these conditions; the mono-silver complex was obtained by adding a chloroform solution of the porphyrin to the solution of silver acetate in glacial acetic acid and heating under reflux. This variant was also useful in those cases where the slight solubility of the porphyrin in glacial acetic acid alone would have required large quantities of solvent. The reaction mixture was examined spectroscopically from time to time; after completion of the reaction the solution was concentrated to a small volume and the crystalline product removed by filtration after cooling.

Method 2 (Weakly Alkaline Medium).—The metal salt was added to the hot solution of the porphyrin in pyridine; the reaction mixture was heated until conversion was complete and concentrated under reduced pressure on a steam-bath to obtain the crystalline product. Thallium yielded two complexes, one relatively labile one directly, and a stabile one when hydrogen peroxide had been added to the reaction mixture.

Method 3 (Strongly Alkaline Medium).—To a porphyrin solution in pyridine the required metal salt and 40% methanolic potassium hydroxide were added.

The acetates of the metals gave the best results in forming the complex salts. Gold chloride ($AuCl_3$) and tin chloride ($SnCl_2$) were used for the preparation of the gold and tin complex salts, respectively. It was best to obtain complete conversion of the free porphyrin into the complex metal salt before attempting to isolate the product. The separation of any free porphyrin remaining as an impurity was usually difficult. This point of complete conversion could be ascertained by diluting a few drops of the reaction mixture with ether (acetic acid present was removed with water) and examining the ether solution spectroscopically for the bands of free T.P.P. In case of their presence the solution had to be refluxed longer, occasionally with the addition of more inorganic salt. In Method 1 above it was sometimes necessary to distil off the chloroform and to reflux the remaining acetic acid solution to obtain complete conversion. In the preparation of the cadmium, lead and thallium complexes a small amount of free T.P.P. always remained in the pyridine mother liquid; however, since these complexes were insoluble in pyridine and crystallized out while the free porphyrin was quite soluble, a good separation was obtained.

Copper Complex Salt. Preparation, (a) Method 1.—T.P.P.,[8] 50 ml. of chloroform, 200 mg. of copper acetate in 50 ml. of glacial acetic acid; yield, quantitative. Recrystallized by extraction from Soxhlet thimble with benzene.

Elimination of Copper from the Complex.—The crystals were moistened with water, and phosphorus pentachloride

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[6] Helberger, *Naturwiss.*, **26**, 316 (1938).

[7] Helberger and Hevér, *Ber.*, **72**, 11 (1939).

[8] 500 mg. T.P.P. was used in each experiment, except where a different amount is mentioned.

TABLE II

ANALYSES, %

Formula	Mol. weight	Calculated							Found					
		C	H	N	Cl	O	Metal	Py[a]	C	H	N	Cl	Metal	Py
$C_{44}H_{28}N_4Cu$	676.26	78.12	4.18	8.29			9.41		78.1	4.4	8.5		9.2	
$C_{44}H_{29}N_4Ag$	721.58	73.23	4.05	7.77			14.95		73.6	3.7	7.9		14.8	
$C_{44}H_{28}N_4Ag_2$	828.45	63.79	3.41	6.76			26.04		63.5	3.5	6.7		25.3	
$C_{44}H_{28}N_4Au_2Cl_4$	1148.92	45.99	2.45	4.89	12.34		34.33		46.4	2.5	4.9	12.8	34.0	
$C_{44}H_{28}N_4Mg$	637.01	82.94	4.43	8.80			3.83		80.4	4.4	8.6		3.8	
$C_{44}H_{30}N_4MgO$	655.03	80.67	4.62	8.56		2.44	3.71		80.4	4.4	8.6		3.8	
$C_{44}H_{28}H_4Zn$	678.07	77.93	4.16	8.27			8.64		77.7	4.3	8.4		10.0	
$C_{44}H_{28}Cd \cdot Py$	804.18	73.18	4.0	8.71			13.98	9.85	72.9	4.0	8.6			9.6
$C_{44}H_{28}N_4Cd$	725.10	72.88	3.89	7.73			15.50		72.9	3.9	7.8			
$C_{44}H_{28}N_4Hg$	813.30	64.97	3.47	6.89			24.67		64.9	3.5	7.0		24.0	
$C_{44}H_{28}N_4Tl$	817.08	64.67	3.45	6.86			25.02		64.0	3.7	6.3		21.0	
$C_{44}H_{28}N_4SnCl_2$	802.30	65.86	3.52	6.98	8.84		14.80		65.5	3.6	7.0	10.0		
$C_{44}H_{28}N_4PbPy$	899.00	65.46	3.70	7.79			23.05		65.3	3.6	7.5		22.3	
$C_{44}H_{28}N_4MnCl$	703.08	75.16	4.01	7.97	5.05		7.82		75.0	4.0	8.1	5.0	7.9	
$C_{44}H_{28}N_4FeCl$	703.99	75.06	7.01	7.96	5.04		7.93		75.1	4.1	8.0	5.1	7.8	
$C_{44}H_{28}N_4Co$	671.63	78.68	4.20	8.34			8.78		78.7	4.2	8.3		8.6	
$C_{44}H_{28}N_4Ni$	671.38	78.71	3.20	8.35			8.74		78.9	4.5	8.3		8.7	

[a] Pyridine.

was added until further addition caused no reaction. The solution was then poured into ether and neutralized with sodium carbonate solution. The ether layer contained the free porphyrin.

(b) **From Formic Acid Solution.**—Constant boiling formic acid, approximately 90% HCOOH, is a good solvent for the free porphyrin. From this solution a complex copper salt of the porphyrin could be obtained which differed from that prepared above, Method 1, in that it possessed an additional intense absorption band at 651.8. T.P.P.[8] was dissolved in 200 ml. of 90% formic acid, 400 mg. of copper acetate was added and the whole refluxed on a steam-bath for one hour. At the end of this time conversion was complete and the yield was quantitative. The analysis of this material, recrystallized from benzene, was identical with that of the copper complex salt prepared under (a).

Mono Silver Complex Salt. Preparation, Method 1.—T.P.P.,[8] 50 ml. of chloroform, 500 mg. of silver acetate, 50 ml. of glacial acetic acid. For analysis the material was recrystallized twice from benzene.

Di Silver Complex Salt.—A silver complex salt containing two atoms of silver in the molecule was obtained from glacial acetic acid solutions with silver acetate. Five hundred ml. of glacial acetic acid containing 150 mg. of the porphyrin was refluxed with 150 mg. of silver acetate for one-half hour; yield, 90 mg. blue violet crystals on cooling.

Gold Complex Salt. Preparation, Method 1.—Two hundred mg. of porphyrin, 50 ml. of chloroform, 200 mg. of gold chloride, 1 g. of sodium acetate, 50 ml. of glacial acetic acid. The chloroform was distilled off and the solution refluxed fifteen minutes, cooled and filtered. Three hundred mg. of blue crystals was obtained. They were recrystallized by extracting from a Soxhlet thimble with a mixture of 20 ml. of chloroform and 50 ml. of benzene; yield, 200 mg. blue-red crystals.

Magnesium Complex Salt, "Phyllin." Preparation, Method 3.—A sealing tube similar to that employed in the synthesis of the porphyrin[1] was filled with the following: 300 mg. of T.P.P. in 25 ml. of hot pyridine, 500 mg. of magnesium acetate, 60 ml. of 40% methanolic potassium hydroxide. The air in the tube was displaced by nitrogen to render sealing safer, and the sealed tube was supported in a large Carius furnace. For this experiment the furnace was tilted at an angle of 30° or more to prevent the porphyrin from creeping into the upper part of the tube not bathed in liquid. The furnace was left at 170° for sixteen hours, then the contents of the cooled tube were poured into approximately 100 g. of ice made from distilled water. When the ice had melted, the crystalline precipitate was filtered off, washed with water, and the crystals dried by suction. This dried material was then recrystallized by extracting from a thimble with 20–30 ml. of ether. The "phyllin" was very photolabile; the reaction mixture or solutions of the "phyllin" should not be exposed to light. The reaction tube was wrapped in towelling on removing from the furnace and the extraction apparatus for recrystallizing was wrapped in black paper, or better still, the extraction was carried on in a dark room. Solutions of the "phyllin" could be exposed for brief periods to diffuse light but a half hour exposure to daylight, not direct sunlight, caused a visible decrease in the intensity of the absorption band at 624.4 mμ. On exposing dilute ether solutions of the "phyllin" to daylight, northern exposure, the first visible change was a decrease in the intensity of the absorption band at 624.4 mμ. After two hours this band had usually disappeared completely. During this time the other absorption bands remained visibly unchanged. On further exposure the "phyllin" slowly decomposed to yield a pale yellow ether solution. Analysis of different batches of the "phyllin," prepared as described above, consistently yielded low values for carbon. Assuming hydrolytic cleavage of one bond from magnesium to nitrogen during the precipitation with ice of the "phyllin" from the reaction mixture and calculating for one hydroxyl group in the molecule, the analysis compares with the new theory as shown in Table II.

Zinc Complex Salt. Preparation, Method 1.—T.P.P.,[8] 50 ml. of chloroform, 250 mg. of zinc acetate, and 250 ml. of glacial acetic acid were refluxed for one hour on the steam-bath, and quantitative yield was obtained; the substance was recrystallized by extracting from a Soxhlet thimble with a mixture of 40 ml. of ether and 20 ml. of methanol.

Cadmium Complex Salt. Preparation, Method 2.—One gram of T.P.P. in 100 ml. of hot pyridine, 800 mg. of cadmium acetate, and 40 ml. of 40% methanolic potassium hydroxide were refluxed for two hours on the steam-bath. To this hot solution 240 ml. of hot water was added, and the contents allowed to cool; yield, 1.5 g. of very fine crystals which were washed several times with 2-ml. portions of cold water, dried and extracted from a Soxhlet thimble with 100 ml. of pure ether. For analysis the material was recrystallized once from ether and dried overnight in a phosphorus pentoxide desiccator; it contained 1 mole of pyridine of crystallization. When dried at 175° for eighteen hours to constant weight in a Pregl block, the substance lost 9.6%, corresponding to the pyridine value (see Table II).

TABLE III

ABSORPTION SPECTRA OF METAL COMPLEX SALTS OF $\alpha,\beta,\gamma,\delta$-TETRAPHENYLPORPHINE

The spectra were visually measured in the conventional manner by determining points of equal intensity at the edges of each absorption band which are given in $m\mu$. The center of the band (absorption maximum) was for symmetrical bands calculated by averaging the two values measured. Unsymmetrical bands are indicated by dashes, *e. g.*, ---546.0 shows that the maximum of intensity is located at 546.0 with the more gradual increase of the intensity toward the red region of the spectrum. In recording the order of intensity (Int.:) marked differences in intensity have been separated by a semicolon.

All solutions of the metal complex salts showed red fluorescence; solutions of the cadmium, stabile thallium, iron chloride, manganese and cobalt complex exhibited it intensely. The red fluorescence was most conspicuous in the solutions of the alkali complexes and of the magnesium and zinc salt.

Name	Solvent	Color of solution	Absorption spectrum
Copper	Ether	Pink	I, 610.6; II, 574.7; III, 538.0; IV, 497.3; E. A. 446.6. Int.: III; I, IV, II
Mono Silver	Ether	Pink	I, 575.3; II, 539.3; III, 501.0; Shadow 477; E. A. 448.0. Int.: II; I, III; IV
Di Silver	Ether	Pink	I, 576.2; II, 539.3; III, 500.5; IV, 474.2; E. A. 448.0. Int.: II; I, III; IV
Gold	Ether	Orange-pink	I, 522.7; II, 485.2; Shadow 458; E. A. 436.5. Int.: I; II
Magnesium ("Phyllin")	Ether	Magenta	I, 651.5; II, 624.4; III, 602.6; IV, 562.3; V, 521.4; VI, 490.2; VII, 461.2; E. A. 441.6. Int.: IV; III; II, V, VII, I, VI
Zinc	Ether	Magenta	I, 595.5; II, 553.9; III, 515.0; IV, 485.3; E. A. 440.5. Int.: II, I; III, IV
Cadmium	Ether	Green	I, 613.4; II, 567.5---; III, 528.2; IV, 497.8; V, 472.7; E. A. 456.0. Int.: II, I; III, IV, V. In greater dilution: Ia, 623.9; Ib, 610.0; Ib > Ia. In very weak solution: VI, 431.5; E. A. 410[a]
Mercury	Benzene	Reddish with tinge of green	I, 653.9; II, 619.0; III, 559.3; IV, 513.9; Shadow 484.8; E. A. 455.3. Int.: III; IV, I, II
	Pyridine	Grass green	I, 629.9; II, 584.6; III, 545.1; Shadow 512; E. A. 482.8. Int.: I, II; III. III
Thallium (labile)	Pyridine	Green	I, 695.8; II, ---645.5---; III, 483.0; IV, 458.3---; E. A.---418.0. Int.: III, IV, I; II
Thallium (stabile)	Pyridine–ether (1:3)	Bluish-green	Shadow 651.0; I, 631.7; II, 606.2; III, 565.3; IV, 526.7; Shadow 495.6; E. A. 447.2. Int.: III, II; I, IV. After 3 hours exposure to bright light: I, 650.9; II, 610.4; III, 567.0; IV, ---518.5; E. A. 460. Int.: III, II; IV, I[b]
Tin Chloride	Pyridine–ether (1:3)	Purple	I, 627.4; II, 601.6---; III, 560.3; IV, 522.2---; V, 490.3; Shadow 460.5; E. A. 444.0. Int.: III, II; I = IV, V[c]
Lead	Ether	Bright Green	I, 657.0; II, ---606.2---; III, 555.8; Shadow 506; IV, 463.4; V, 438.4; E. A. 420. Int.: IV, V; I; II, III
Manganese	Ether	Green	I, 619.9; II, 579.9---; III, 532.0; E. A. 492.5. Int.: I, II, III. In greater dilution: IV, 473.7; E. A. Approx. 420
Iron Chloride ("Hemin")	Pyridine–ether or in benzene	Orange-brown	I, 687.9---; II, ---571.6---; III, ---506.6---; E. A. 465.2. Int.: III; II, I
Cobalt	Ether	Orange	I, 607.7; II, ---626.6---; E. A. ---447.0. Int.: II; I
Nickel	Pyridine–ether (1:4)	Pink	I, 652.1; II, ---614.1; III, 557.1; IV, ---526.3; V, 485.9; E. A. 455. Int.: IV; II, III, V
Lithium	Pyridine–methanol	Magenta	I, ---619.2; II, 575.5; III, 533.6; IV, 502; E. A. 456.3. Int.: I, II, III, IV
Sodium	Pyridine–methanol	Magenta	I, 626.3; II, 580.8; III, 539.7; Shadow 506; E. A. 462.8. Int.: I, II, III
Potassium	Pyridine–methanol	Magenta	I, 626.5; II, 580.2; III, 540.2; IV, 492.6; E. A. 458.2. Int.: I, II; IV, III
Rubidium	Pyridine–methanol	Green	I, ---634.0; II, 589.2; III, 549.6; E. A. 567.2. Int.: I, II; III
Cesium	Pyridine–methanol	Green	I, 651.7; II, 599.1; III, 554.4; IV, 516.4; E. A. 472.8. Int.: I, II; III, IV

[a] In pyridine solution the absorption bands are slightly shifted toward the red region. [b] This change did not occur in the dark. [c] In the pyridine mother liquid above remained a small amount of a substance of bluish lavender color in pyridine–ether solution. Spectroscopically it showed an additional absorption band at 651.4 and a more intense 627.4 band.

Mercury Complex Salt. Preparation, Method 2.—T.P.P.,[8] 50 ml. of pyridine and 500 mg. of mercuric acetate were refluxed for two and one-half hours on a steam-bath. The conversion was complete and yielded approximately

0.5 g. of blue needles from the solution after cooling. The substance was recrystallized twice from benzene by extracting from a Soxhlet thimble and air dried.

The spectra in benzene and in pyridine are recorded in Table III. In piperidine and quinoline the absorption spectrum was similar to that in pyridine, the only difference lying in a shift of the absorption bands toward the red, this shift being greatest for piperidine. The color and spectrum shifted to that observable in the organic base if a drop of the base was added to the benzene solution.

Labile Thallium Complex Salt. Preparation, Method 2.—Two hundred mg. of T.P.P., 20 ml. of pyridine and 200 mg. of thallous acetate were refluxed overnight on a steam-bath. One hundred mg. of dark green crystals was obtained from the cold solution. Addition of more thallous acetate to the mother liquid and repeating the refluxing yielded a second crop of complex salt. This thallium complex was very unstable in solution, the mother liquid always containing unchanged porphyrin. When the above green crystals were dissolved in pyridine, the free T.P.P. spectrum appeared immediately in the spectrum of the salt. A pure complex salt spectrum was obtained only in hot pyridine solution in the presence of thallous acetate. On standing the free porphyrin spectrum appeared in this solution also. The complex was easily split by water to form the free porphyrin.

Stable Thallium Complex Salt. Preparation, Method 2.—The thallous acetate used must be oxidized in order to prevent the formation of the unstable thallium complex described above. The thallous salt was oxidized in acetic acid with 30% hydrogen peroxide solution, and the crystals obtained on evaporating the solution were used, or 30% hydrogen peroxide was added directly to a pyridine solution of the porphyrin containing thallous acetate. Both methods were used, the latter being described below. A solution of T.P.P.,[8] 50 ml. of pyridine, 500 mg. of thallous acetate and 2 ml. of 30% hydrogen peroxide boiled down to a total volume of 30 ml. After addition of 20 ml. of pyridine and 1 ml. of 30% hydrogen peroxide solution and concentrating to 20 ml. by boiling, the conversion was complete. Forty ml. of hot methanol was poured into the hot solution. Five hundred mg. of lustrous blue crystals formed on cooling. The material was extracted from a Soxhlet thimble with benzene, filtered, the benzene solution concentrated to 20 ml., and 50 ml. of hot methanol added; yield, 450 mg.

Tin Chloride Complex Salt. Preparation, Method 2.—T.P.P.[8] in 50 ml. of pyridine and 400 mg. of stannous chloride: Refluxing for two hours yielded 500 mg. of fine lavender crystals on cooling, which were recrystallized by extracting from a thimble with a mixture of 15 ml. of chloroform and 40 ml. of benzene.

Lead Complex Salt. Formation, Method 2.—T.P.P.,[8] 50 ml. of pyridine, and 500 mg. of lead acetate were heated for one hour. On cooling approximately 500 mg. of dark blue-green crystals was obtained and recrystallized twice by extracting from a thimble with 40 ml. of benzene. The analytical results check for 1 mole of pyridine in the molecule. There was no loss in weight upon heating at 175° for eighteen hours.

Manganese Chloride Complex Salt. Formation, Method 1.—T.P.P.,[8] 50 ml. of chloroform, 70 ml. of glacial acetic acid, 500 mg. of manganous acetate and 100 mg. of sodium chloride were refluxed for six hours. The solvents were distilled off under vacuum and 50 ml. of glacial acetic acid was added to the dry residue and the resulting solution concentrated to approximately 15 ml. The crystals in the cooled solution were filtered off, washed with glacial acetic acid, air dried, and recrystallized by extracting from a Soxhlet thimble with ether; yield, approximately 300 mg. of dark green crystals of high luster. The manganese chloride complex was extremely soluble in methanol. Crystals could be obtained if the methanol solution was added to ligroin and the methanol evaporated. The spectrum of the resulting crystals in methanol differed little from that in ether, which is given in Table III.

Iron Chloride Complex Salt, "Hemin." Preparation, Method 1.—T.P.P.[8] was dissolved in 50 ml. of chloroform and 200 mg. of sodium chloride was added. Into this solution was filtered, hot, 150 ml. of glacial acetic acid saturated with ferrous acetate. This was prepared by dissolving pure iron filings in boiling glacial acetic acid and filtering the hot solution into the chloroform. After refluxing for two hours, concentrating to approximately 50 ml., cooling and filtering, approximately 500 mg. of impure crystals was obtained. The crystals were extracted from a thimble with chloroform, the solution concentrated to 10 ml. and approximately 80 ml. of hot methanol was added. Dark blue crystals formed on cooling. Prolonged heating had to be avoided since this caused the formation of a substance with spectrum differing from that given above for the "hemin." For analysis the material was recrystallized twice from chloroform-methanol.

Cobalt Complex Salt. Preparation, Method 1.—T.P.P.,[8] 50 ml. of chloroform, 250 mg. of cobaltous acetate, and 50 ml. of glacial acetic acid were refluxed for one-half hour. On cooling fine maroon crystals formed quantitatively and were recrystallized by extracting from a thimble with ether.

Nickel Complex Salt.—Nickel acetate was substituted for cobalt acetate in the above procedure and the solution was heated for one hour. Five hundred ten mg. of blue crystals, filtered from the cooled solution, were recrystallized by extracting from a thimble with benzene.

Lithium Complex Salt. Formation.—A methanolic solution of lithium hydroxide was added to a solution of the porphyrin in pyridine.

Sodium Complex Salt. Formation.—Same as above, substituting sodium hydroxide for the lithium salt.

Potassium Complex Salt. Preparation.—50 mg. of T.P.P. in 20 ml. pyridine was added to 20 ml. of 40% methanolic potassium hydroxide. After a few hours of standing the solution was filtered through a fritted glass filter. It was not possible to prepare the pure complex salt since it was unstable in solutions not containing dissolved potassium hydroxide.

Rubidium Complex Salt. Formation.—A methanolic solution of rubidium hydroxide was added to a solution of the porphyrin in pyridine. The hydroxide was obtained by shaking rubidium chloride with silver oxide in methanol.

Cesium Complex Salt. Formation.—Same as above, substituting cesium hydroxide for rubidium hydroxide.

Summary

1. The preparation of the complex salts of $\alpha,\beta,\gamma,\delta$-tetraphenylporphine with the following metals is reported: lithium, sodium, potassium, rubidium, cesium, copper, mono silver, di silver, gold chloride, magnesium ("phyllin"), zinc, cadmium, mercury, tin chloride, lead, thallium (stabile complex salt), thallium (labile complex salt), manganese chloride, ferric chloride ("hemin"), cobalt and nickel.

2. The data for the absorption spectra of these compounds in the visual region of the spectrum are presented.

3. The elementary analyses by microanalytical procedures show that most of these salts are normal complexes; the gold salt crystallizes from benzene with 1 mole of gold chloride, the "phyllin" as magnesium hydroxide, cadmium and lead salt with 1 mole of pyridine. The structure of the tin chloride complex remains to be investigated further. The isolation and analysis of the complexes of the alkali metals—for which the spectra only are given—have not been performed as yet.

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