dry hydrogen bromide was added dropwise with stirring. The green color of the initial solution lightened gradually while a pale green precipitate increased.

Dibromo(acetylacetonato)(acetylacetone)chromium(III), $CrBr_2(acac)(acacH)$.—In a similar fashion as above 1.5 g (4.3 mmol) of tris(acetylacetonato)chromium(III) was dissolved in dichloromethane containing 20 g (200 mmol) of acetylacetone and allowed to react with 25.8 mmol of dry hydrogen bromide in dichloromethane. The reaction mixture was kept standing overnight to increase the amount of the pale green precipitate.

Dichloro(acetylacetonato)(acetylacetone)chromium(III), $CrCl_2(acac)(acacH)$.—According to the literature,[29] except for exclusion of zinc powder, anhydrous chromium(III) chloride was allowed to react with dry tetrahydrofuran in a Soxhlet extractor to produce trichlorotris(tetrahydrofuran)chromium(III). About 1 g of the purple complex $CrCl_3(THF)_3$ was dissolved in about 8 ml of acetylacetone. Hydrogen chloride gas was evolved resulting in a dark green solution, to which about 30 ml of dry petroleum ether was added to separate $CrCl_2(acac)(acacH)$ as a pale green precipitate.

All these novel complexes are very hygroscopic and were transferred from the reaction vessel *via* polyethylene tubing to a filtration apparatus set up in a desiccator containing phosphorus pentoxide. They were washed with petroleum ether and dried *in vacuo*.

Analyses and Measurements.—Metal contents in these complexes were determined gravimetrically: cobalt and manganese as sulfates, nickel as the bis(dimethylglyoximato) complex, and zinc as ammonium phosphate. Halogens were also determined gravimetrically as silver salts.

Absorption spectra of solutions were obtained using a Hitachi EPS-3T recording spectrophotometer. A solid specimen was ground with Nujol and placed between two plates of opal glass, and its transmission spectrum was measured[30] with a Hitachi Perkin-Elmer spectrophotometer, Model 139. The infrared spectra of solid specimens were measured in Nujol by means of Hitachi EPI-2 (4000–700 cm^{-1}), EPI-L (700–200 cm^{-1}), and FIS-3 (400–30 cm^{-1}) infrared spectrophotometers.

A C-282 Thermo-Spring balance of Hamada Denki Seisakusho, Ltd., was used for the thermogravimetric analysis, and the temperature of a sample was raised at a rate of 20 or 30°/hr *in vacuo*. The volatile decomposition product was collected in a trap cooled with Dry Ice–methanol and submitted to the gas chromatographic analysis. A column of Apiezon L grease carried on Neosorb NC (Nishio Industries Co., Ltd.) was employed at 100° on which hydrogen gas was passed at a flow rate of 40 cm^3/min. On the other hand, the solid decomposition residue was dissolved in water and analyzed.

The magnetic susceptibility was determined at room temperature by the Gouy method with an automatically recording magnetic balance (Shimadzu Seisakusho Co., Ltd.). The sample was put into a tube (3 mm in diameter and 20 mm in length) quickly. Hexaamminechromium(III) chloride and mercury(II) tetraisothiocyanatocobaltate(II) were used as reference compounds.

Acknowledgments.—We are indebted to Dr. Hanako Kobayashi of Kyoto University for her help in magnetic measurements and also to Mr. J. Gohda for the elemental analyses. Financial aid by the Ministry of Education and kind supply of acetylacetone by Daicel Co., Ltd., are also acknowledged.

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[29] R. J. Angelici, "Synthesis and Technique in Inorganic Chemistry," W. B. Saunders, Philadelphia, Pa., 1969, p 51.

[30] K. Shibata, *Methods Biochem. Anal.*, **7**, 77 (1959).

CONTRIBUTION FROM THE SCHOOL OF CHEMICAL SCIENCES AND THE MATERIALS RESEARCH LABORATORY,
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Phthalocyanine Derivatives from 1,2,4,5-Tetracyanobenzene or Pyromellitic Dianhydride and Metal Salts

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Two general methods have been reported for the preparation of fused-ring polymeric phthalocyanines. These preparations involve the reaction of tetrafunctional benzene [1,2,4,5-tetracyanobenzene (TCB) or pyromellitic dianhydride (PMDA)] with metal salts, so that the ideal products of such reactions would be sheet-type polymers in which each benzene ring is fused into two phthalocyanine rings. The products of the above reactions now have been investigated. It has been found that (1) the work-up procedures described in the literature for the reactions do not produce pure compounds; (2) the pure compounds which were produced in the present investigation from the reaction of TCB with metal salts are monomeric phthalocyanine derivatives with imide or carboxylic functional groups on the available peripheral sites; (3) the products of the reaction using PMDA are polymeric phthalocyanines, but they are quite impure and probably have only imide functional groups on the peripheral positions rather than carboxylic acid groups as previously described. In the procedure by which the structural assignments were made in this work, hydrolysis derivatives of the complexes are first prepared (thus converting all imide functional groups to carboxylic acid groups); then each complex and its hydrolysis derivative are compared by means of their elemental analyses and infrared spectra. The structures may be inferred by interpretation of these comparative data.

Introduction

The polymeric phthalocyanines have attracted a good deal of attention in recent years. Work in this area has evolved along three principal structural themes. The first (and more common) type of polymer involves the bridging of phthalocyanine units by exocyclic groups attached to the benzene rings (Figure 1a). The second type is one in which a single benzene ring is fused into two phthalocyanine cycles[1,2] (Figure 1b). In a third type, the central metal ions are bridged by oxygen atoms to form the polymeric linkages.[3,4] This gives a stacked polymer rather than a sheet polymer.

[1] H. Inoue, Y. Kida, and E. Imoto, *Bull. Chem. Soc. Jap.*, **38**, 2214 (1965).

[2] W. C. Drinkard and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 4795 (1959).

[3] P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1719 (1936).

[4] T. R. Janson, A. R. Kane, J. F. Sullivan, K. Knox, and M. E. Kenney, *J. Amer. Chem. Soc.*, **91**, 5210 (1969).

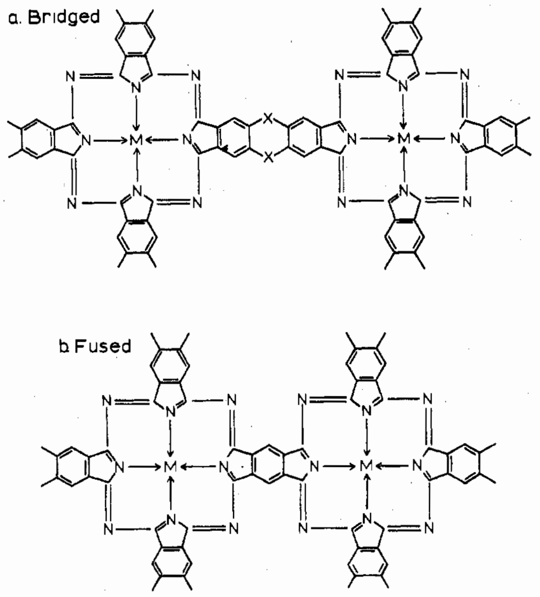
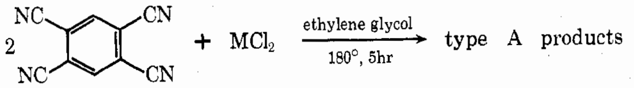


Figure 1.—Types of phthalocyanine polymers.

A number of preparative methods for the first two polymeric types have been reviewed.[5] It is evident that the reaction products have in most instances been investigated for possible practical value (*i.e.*, as pigments or heterogeneous catalysts). However, the proposed structures of the products have in general been very poorly substantiated. This lack of structural data is undoubtedly due to the fact that the materials are amorphous and insoluble.

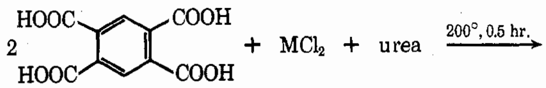
In the present work, the structures of some complexes for which "fused ring" (Figure 1b) polymeric structures had been claimed have been investigated, and the results indicate that the structures previously assigned to the compounds are substantially incorrect.

Two general synthetic routes have been devised for the preparation of these compounds, and the present work includes studies of compounds prepared by both methods. The first group of compounds studied was prepared by the method shown in eq 1. This method, devised and extensively utilized by Inoue and co-workers,[1,6–8] is of especial interest because the activity of the reaction products as oxidation catalysts was reported by Inoue, *et al.*, to be dependent on the presence of ions of two different metals, one of which must be iron.[6] Furthermore, the activity was found to vary (somewhat erratically) with the C:N ratio in the compounds. When the present authors undertook to determine the structural factors which control the catalytic activity of the compounds, it was found that the purification procedures described by Inoue, *et al.*, were not effective in our hands and that the compounds prepared according to their instructions were thus quite impure. When the compounds of type A were purified, they were found to be monomeric species and not the polymers expected from Inoue's report.[6]



$$2\ \begin{matrix}\mathrm{NC} & & \mathrm{CN}\\ \mathrm{NC} & & \mathrm{CN}\end{matrix} + \mathrm{MCl_2} \xrightarrow[180°,\ 5\mathrm{hr}]{\text{ethylene glycol}} \text{type A products} \qquad (1)$$

Our discovery that the type A compounds are not polymers led us to investigate the products produced by the method of eq 2. The products produced by this method were described by Drinkard and Bailar in 1959.[2] In their paper, the structures of the compounds were rationalized by elemental analysis as short-chain polymers (oligomers) which contained only carboxylic acid functional groups. However, compounds of type B prepared by their method turned out also to be quite impure. The present results show that B-type compounds probably contain imide functional groups rather than acid groups; nevertheless, they do appear to be chain-type oligomers of two to five units.



$$2\ \begin{matrix}\mathrm{HOOC} & & \mathrm{COOH}\\ \mathrm{HOOC} & & \mathrm{COOH}\end{matrix} + \mathrm{MCl_2} + \text{urea} \xrightarrow{200°,\ 0.5\ \mathrm{hr.}} \text{type B products} \qquad (2)$$

Methodology

Since the phthalocyanines with which this study deals are insoluble in all solvents except those which are very acidic (*i.e.*, concentrated H_2SO_4) or very basic (*i.e.*, 25% aqueous KOH), and all of the compounds react with these solvents, solution techniques for the measurement of physical properties are not applicable. Furthermore, such solid-state measurements as X-ray powder patterns and electronic spectra are not useful in ascertaining the detailed structures of the complexes. In fact, the only useful investigative tools were found to be (a) elemental analyses, (b) infrared spectra, and (c) the preparation of derivatives.

The use of these tools in analyzing the structures of the complexes requires several points of clarification. The following should be understood.

(1) Since tetrafunctional benzene is used in the synthesis of both type A and type B complexes, certain functional groups will be present at peripheral points where the benzene ring is not fused into two phthalocyanine rings. These functional groups may be carboxylic acids, imides, or amides (Figure 2).

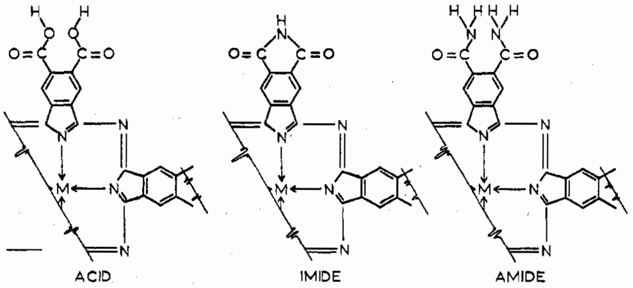


Figure 2.—Peripheral functional groups on phthalocyanine derivatives.

(2) The presence (or absence) of these functional groups may be determined from the infrared spectra, since each type of functional group gives a characteristic pattern in the region 1600–1800 cm^{-1} (Figure 3). In practice, only the imide and carboxylic acid func-

(5) F. H. Moser and A. L. Thomas, "Phthalocyanine Compounds," Reinhold, New York, N. Y., 1963; A. A. Berlin and A. I. Sherle, *Inorg. Macromol. Rev.*, **1**, 235 (1971).

(6) H. Inoue, Y. Kida, and E. Imoto, *Bull. Chem. Soc. Jap.*, **40**, 184 (1967).

(7) H. Inoue, Y. Kida, and E. Imoto, *ibid.*, **41**, 684 (1968).

(8) H. Inoue, Y. Kida, and E. Imoto, *ibid.*, **41**, 692 (1968).

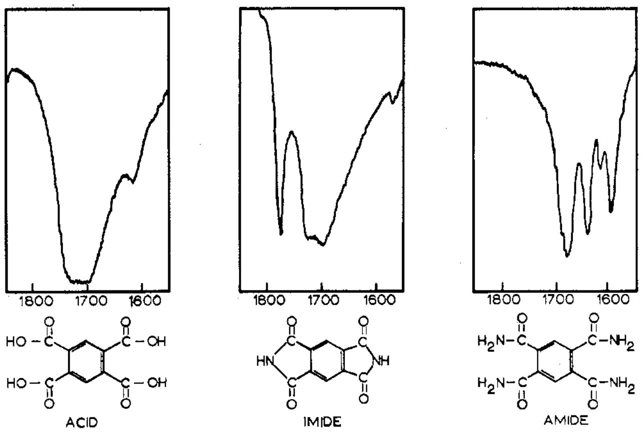


Figure 3.—Infrared spectral bands due to functional groups on tetrasubstituted benzene.

tionalities have been found in reaction products, so the subsequent discussion will be limited to compounds containing only these two groups.

(3) The carbon:nitrogen and nitrogen:metal ratios in the complexes depend on two factors: the size and shape of the oligomer and the type of peripheral functional groups present. For acid groups, the appropriate C:N and N:M ratios are listed in Table Ia and for imides, Table Ib. It will be noted that the differences in the ratios are most dramatic for the very short oligomers (two or three units) and for the compounds with acid functional groups.

TABLE I

CALCULATED CARBON:NITROGEN AND NITROGEN:METAL RATIOS FOR POLYMERIC PHTHALOCYANINE DERIVATIVES

No. of phthalocyanine units	a Acid end groups C/N	 N/M	b Imide end groups C/N	 N/M
1	5.00	8.0	3.33	12.0
2	4.37	8.0	3.18	11.0
3	4.16	8.0	3.11	10.7
4 (linear)	4.06	8.0	3.10	10.5
5 (linear)	4.00	8.0	3.08	10.4
6 (linear)	3.96	8.0	3.00	10.0
∞ (linear)	3.75	8.0	3.00	10.0
4 (sym)	3.75	8.0	3.00	10.0
5 (unsym)	3.75	8.0	3.00	10.0
∞ (sym)	2.50	8.0	2.50	8.0

(4) If a mixture of acid and imide functional groups is present in the complex, the size of the oligomer cannot be determined directly by elemental analysis and the infrared spectrum. However, by hydrolysis under very stringent conditions, the imide groups in such a "mixed" complex can be converted to acid groups, thus making, in effect, an all-acid derivative of the "mixed" complex. Comparison of the C:N and N:M ratios of the mixed complex and its derivative allow one to deduce both the number of units in the oligomer and the acid:imide ratio of functional groups in the complex.

This comparative process yields quite exact results for compounds which contain three or fewer phthalocyanine rings in an average molecule. However, if "large" polymers should be encountered (eight or more units in a molecule), the above process would allow only a rough estimate of size.

The chemical procedures utilized in establishing the structures of the phthalocyanine complexes fall into two categories. One set of procedures (solvent washing, acid extraction) is simply for purification of the complexes. The second category consists of reactions designed to prepare chemical derivatives.

A general method for identifying type A complexes has evolved from the chemical procedures and the physical measurements as follows: the crude reaction product is washed with acetone–water mixtures until all of the extraneous organic matter has been removed; the complex is then extracted repeatedly with dilute HCl solution to remove metal ions not contained within the phthalocyanine rings; and the complex is subjected to hydrolysis in hot 50% KOH to convert the imide functional groups to acids. After each chemical step, the product is identified by elemental analyses and interpretation of its infrared spectrum.

While use of the above method can and does result in unequivocal identification of the complexes in most cases, there are some definite limitations to its application. These limitations arise from the fact that the chemical stabilities of the complexes vary with the core metal, the stability decreasing in the order Cu > Fe > Mo. Thus, the copper complexes are stable to all of the chemical procedures, whereas those containing iron are not stable toward hydrolysis, and those containing molybdenum are not stable to acid washing. Since the data are complete for the copper complexes, structural deductions concerning the complexes containing iron and molybdenum are based to a certain degree on analogy with the copper compounds. Use of this analogy is strongly supported by the similarity of preparation and by the infrared spectra.

Experimental Section

Equipment.—All solvents and metal salts were commercially available and of reagent grade. Pyromellitic acid was purchased from Aldrich Chemical Co. and pyromellitic anhydride from Eastman Organic Chemicals. The 1,2,4,5-tetracyanobenzene was prepared from pyromellitic acid through the tetramide[9] by the method of Lawton and McRitchie.[10] Infrared spectra were recorded on a Perkin-Elmer 457 infrared spectrophotometer as Nujol mulls. Elemental analyses were performed by the microanalytical laboratory at the University of Illinois.

Preparations.—The following type A compounds were prepared under identical reaction conditions and work-up procedures as follows.

A 50-ml, round-bottomed flask with a 14/20 neck was charged with 20 ml of ethylene glycol, TCB, and metal salt. The flask was fitted with a reflux condenser and the reaction mixture was heated, with stirring, to 190° for 5 hr, after which the black suspension was diluted with 100 ml of water and filtered by suction on a sintered glass filter. The solid was then washed with 50 ml of acetone and dried in air. Subsequently, the solid was crushed to a powder and stirred in a mixture of 35 ml of water and 65 ml of acetone for 0.5 hr, filtered, washed with acetone, and dried in air. This procedure was repeated at least three times and up to six times if the washings remained colored. At this point, a portion of each complex was dried at 0.2 Torr over P_4O_{10} and analyzed (Table II).

Next, each complex was slurried with 100-ml portions of 0.01 *N* HCl solution for 15 min, then filtered, washed with water and acetone, and dried in air. This procedure was repeated until metal ions could no longer be detected in the washings (usually three or four times). Visual qualitative tests for metal ions were the following: for copper, treatment of the solution with ammonia; for iron, addition of NaSCN. Again at this point, the compound was dried and analyzed (Table III).

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[9] H. Meyer and K. Steiner, *Monatsh. Chem.*, **35**, 391 (1914).

[10] E. A. Lawton and D. D. McRitchie, *J. Org. Chem.*, **24**, 26 (1959).

TABLE II

ELEMENTAL ANALYSES (%) OF SOLVENT-WASHED TYPE A COMPLEXES

	1-A	**2**-A	**3**-A		**4**-A	**5**-A
	Found	Found	Found	Calcd	Found	Found
C	51.54	44.45	54.03	54.49	51.07	40.89
H	2.36	2.87	2.67	1.71	2.67	2.65
N	16.58	13.00	17.33	17.48	16.43	10.52
Cu	14.61	4.16				
Fe		13.06	6.32	6.34	5.01	
Mo					13.83	22.57

TABLE III

ELEMENTAL ANALYSES (%) OF ACID-WASHED TYPE A COMPLEXES

	1-A		**2**-A		**3**-A	**4**-A
	Found	Calcd	Found	Calcd[a]	Found	Found
C	56.08	56.36	55.05	55.27	54.05	52.13
H	2.49	1.42	2.79	1.50	2.48	2.68
N	19.96	19.72	17.91	17.73	16.55	18.76
Cu	6.81	7.46	5.52	5.48		
Fe			1.54	1.61	4.97	4.83
Mo						1.54

[a] Percentages of copper and iron are calculated on the basis of Cu = 75% of total metal and Fe = 25%.

TABLE IV

QUANTITIES OF REAGENTS USED IN PREPARING TYPE A COMPLEXES

	Ethylene glycol, ml	TCB, g (mmol)	$CuCl_2 \cdot 2H_2O$,[a] g (mmol)	$FeCl_3 \cdot 6H_2O$,[a] g (mmol)	Ammonium heptamolybdate, g (mequiv)
1-A	40	1.78 (10)	0.85 (5)		
2-A	20	0.89 (5)	0.12 (0.75)	0.68 (2.5)	
3-A	40	1.78 (10)		1.35 (5)	
4-A	40	1.78 (10)		0.68 (2.5)	0.44 (2.5)
5-A	20	0.89 (5)			0.44 (2.5)

[a] Anhydrous copper chloride or ferric chloride may be substituted for the hydrated salts with no appreciable change in results.

The above procedures provide complete purification for the type A complexes which contain copper. Complexes which contain iron and/or molybdenum are not stable toward the acid-washing step. For complexes found to be pure, calculated analyses are given in Tables II and III. The quantities of TCB and metal salts used in the reactions are shown in Table IV. The empirical and structural formulas on which the calculated values in Table II and III are based are given as follows: **1**-A (Table III), calcd formula $CuC_{40}H_{14}N_{12}O_9$, copper phthalocyaninetetraimide monohydrate; **2**-A (Table III), calcd formula $MC_{40}H_{13}N_{11}O_{10}$, copper iron phthalocyaninetriimidedicarboxylic acid; **3**-A (Table II), calcd formula $FeC_{40}H_{15}N_{11}O_{11}$, iron phthalocyaninetriimidedicarboxylic acid monohydrate.

The hydrolysis experiment was successfully applied to the **1**-A (copper) and **2**-A (copper–iron) complexes (Table III). The reaction and work-up conditions were identical for the two complexes.

A 50-ml Teflon beaker was charged with 20 g of KOH, 20 ml of water, and 0.5 g of acid-washed type A complex. The beaker was covered with a watch glass, and the mixture was heated, with stirring, for 8–10 hr at 100°. The reaction mixture was then diluted with 100 ml of water, filtered through a sintered glass funnel, and slowly acidified to about pH 2 with concentrated (12 *N*) HCl. At this point, the product completely precipitated as a blue, flocculent solid. This was allowed to settle, and most of the supernatant liquid was decanted. The solid was then separated on sintered glass, washed with two 20-ml portions of 0.10 *N* HCl and then with acetone and ether, and dried in air. The solid reaction product is blue, with a red-bronze reflex. It is quite soluble in water, although it dissolves slowly, and it is somewhat soluble in acetone. It is, however, insoluble in acidic aqueous solutions. Each complex was identified as a monomeric octacarboxylic acid phthalocyanine derivative by elemental analysis.

Anal. Calcd for **1**-A, $CuC_{40}H_{16}N_8O_{16}$: C, 51.74; H, 1.74; N, 12.07; Cu, 6.84. Found: C, 51.98; H, 2.44; N, 12.35; Cu, 6.49. Calcd for **2**-A, $Cu_{0.73}Fe_{0.27}C_{40}H_{16}N_8O_{16} \cdot 5H_2O$: C, 47.25; H, 2.57; N, 11.02; Cu, 4.56; Fe, 1.48. Found: C, 47.82; H, 2.26; N, 10.40; Cu, 4.55; Fe, 1.71.

Type B Complexes.—Preparations for type B complexes followed the procedure outlined by Drinkard and Bailar.[2]

A 100-ml 24/40 flask was charged with an intimately ground mixture of anhydrous $CuCl_2$, pyromellitic anhydride, urea, and ammonium molybdate. The flask was fitted with a condenser and immersed in a silicone oil bath, which was then heated to temperatures as noted below for the individual preparations, and held there until the reaction mixture was fused. The black, fused solid was then cooled and washed with three 100-ml portions of water, after which it was crushed, removed from the flask, filtered, washed with acetone, and dried in air. Next, the crushed solid was stirred three times for 30-min intervals with 100-ml portions of 6 *N* HCl solution, and the supernatant liquid was decanted each time. Finally, the solid was hydrolyzed by the same method described for the type A complexes.

Quantities of reagents are given below, as well as empirical formulas, where applicable. Analytical results are in Table V.

1-B: 4.0 g of $CuCl_2 \cdot 2H_2O$ (23.5 mmol), 2.5 g of PMDA (11.5 mmol), 13.0 g of urea (0.22 mol), 0.10 g of ammonium molybdate; heated to 250°; formula $CuC_{40}H_{16}N_8O_{16}$, copper phthalocyanine monomer.

2-B: 2.0 g of $CuCl_2$ (15.0 mmol), 2.5 g of PMDA (11.5 mmol), 13.0 g of urea (0.22 mol), 0.10 g of ammonium molybdate; heated to 180°; formula $CuC_{35}H_{23}N_8O_{17}$, copper phthalocyanine dimer pentahydrate.

3-B: 2.0 g of $CuCl_2$ (15.0 mmol), 2.5 g of PMDA (11.5 mmol), 52.0 g of urea (0.88 mol), 0.10 g of ammonium molybdate; heated to 250°; formula $CuC_{32.5}H_{15.5}N_8O_{12}$, copper phthalocyanine tetramer dihydrate.

4-B: 2.0 g of $CuCl_2$ (15.0 mmol), 2.5 g of PMDA (11.5 mmol), 13.0 g of urea (0.22 mol), 0.10 g of ammonium molybdate; heated to 250°; formula $CuC_{32}H_{15.2}N_8O_{11.6}$, copper phthalocyanine pentamer dihydrate.

TABLE V

ELEMENTAL ANALYSES (%) OF HYDROLYZED TYPE B COMPLEXES

	C		H		N		Cu	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
1-B	50.22	51.74	2.08	1.74	12.12	12.07	6.33	6.84
2-B	47.16	47.15	2.63	2.60	12.58	12.57	7.75	7.13
3-B	50.22	50.45	2.41	1.95	14.35	14.48	5.40	8.21
4-B	50.65	50.50	2.22	1.99	14.87	14.73	6.98	8.35

Results and Discussion

A. Type A Complexes.—Since the preparations of the monomeric type A compounds involve several steps and span a number of compounds, it is convenient to express these results in tabular form. In Table VI, the elemental analyses of some exemplary compounds[11] are summarized for each procedural step in the form of the C:N and N:M ratios.[12]

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(11) The copper–iron complex was prepared as a duplicate of one of Inoue's compounds (no. 5-A, ref 4) with reactants in the relative ratios 5 TCB:2.5 Fe:0.75 Cu, whereas the other four were all prepared using 2 mol of TCB/mol of total metal ion.

(12) The relative error in the ratios is twice as great as that in the analyses themselves. Despite this distortion, the ratios are utilized because they are more easily interpreted than the percentage compositions.

TABLE VI

SUMMARY OF ATOMIC RATIOS FOR TYPE A COMPLEXES[a]

	Procedural step					
	Solvent washing		Acid (HCl) washing		Hydrolysis	
	C/N	N/M	C/N	N/M	C/N	N/M
1-A (copper)	3.40	5.15	3.30	12.2	4.91	8.6
2-A (copper-iron)	4.00	3.10	3.59	11.2	5.26	7.3
3-A (iron)	3.64	10.95	3.67	13.56	...	...
4-A (iron–molybdenum)	3.63	5.0	3.24	13.1	...	...
5-A (molybdenum)	4.53	3.2	...	...	...	...

[a] The experimental error in these ratios is ±5% of the numerical values.

Inspection of Table VI reveals some interesting patterns in the chemical behavior of the complexes. First, it is apparent that the solvent washing procedures leave more metal in the solid material than would be required for coordination in phthalocyanine rings, except in the case of the iron complex. This "excess" metal may be removed by washing the compounds in 0.1 *N* HCl. Analytical data taken before and after acid washing indicate that metal is bound in the solid in two different ways: there are metal ions that are coordinated in the "core" of the phthalocyanine rings, and which cannot be washed out with 0.1 *N* HCl, and metal ions which may be removed by 0.1 *N* HCl but not by water. The latter metal ions are thought to be bound peripherally to deprotonated functional groups on the phthalocyanine rings. These chemically different metal ions will be referred to as the "core" and "peripheral" ions, respectively.

Inspection of Tables II and III further shows that, when a mixture of two metals is present, one metal is preferentially removed by acid washing. This implies that the metal which is *not* removed is preferentially bound as the core metal. In the case of the copper–iron complex, it is evident that copper is preferred as the core metal. Similar behavior is found for the iron–molybdenum complex, except that iron is the preferred core metal.

Since all of the type A complexes contain at least some imide groups, hydrolysis experiments were required to determine the size of the molecules (see Methodology section). As was previously mentioned, these experiments could not be applied to all of the compounds under investigation; however, in the cases of the copper and copper–iron compounds, unequivocal results were obtained. Examination of the infrared spectra (Figure 4) of these two compounds before and after hydrolysis, combined with the clear results of the elemental analyses (Table I and VI), show that the copper and copper–iron hydrolysis products are monomeric phthalocyanine complexes, with eight carboxylic acid end groups. Given that the copper and copper–iron complexes are monomers, the "mix" of acid and imide end groups in the acid-washed complexes may be deduced by reference to Table VII. For the copper complex, a C:N ratio of 3.30 and N:M ratio of 12.2 indicate a tetraimido complex. For the copper–iron complex, ratios of 3.59 (C:N) and 11.2 (N:M) indicate a "mixed" monomer, containing, on the average, three imide groups and two acid groups.

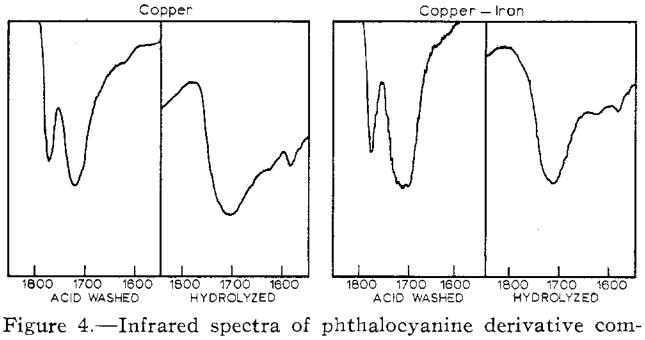

Figure 4.—Infrared spectra of phthalocyanine derivative complexes before and after hydrolysis.

TABLE VII

C/N AND N/M RATIOS FOR MIXTURES OF IMIDE AND ACID FUNCTIONAL GROUPS IN MONOMERIC PHTHALOCYANINE DERIVATIVES

	4 imide	3 imide 2 acid	2 imide 4 acid	1 imide 6 acid	8 acid
C/N	3.33	3.63	4.00	4.44	5.00
N/M	12.0	11.0	10.0	9.0	8.0

Because the iron and iron–molybdenum complexes decompose when hydrolysis is attempted, the complexes cannot be proved to be monomers. However, if one assumes them to be monomers, several conclusions can be drawn from the data in Table VI. By comparison of the C:N and N:M ratios with those in Table VII, the iron complex is found to have three imide and two acid groups, and the iron–molybdenum complex is apparently a tetraimido complex. The N:M ratios of the acid-washed iron and iron–molybdenum complexes show that acid washing leaves an insufficient amount of core metal in the complex. This could be due either to incomplete filling of the rings during preparation or to slow removal of the core metal by acid. In any case, the fact that these complexes are less stable than those containing copper is in accordance with the chemical stabilities of ordinary phthalocyanine complexes.[13]

In addition to the structural findings, the experimental data allow some interesting conclusions concerning the competition between copper and iron in the formation of phthalocyanine derivatives. For example, calculation of the mole equivalent quantity of copper in the crude product **2**-A indicates that all of the reactant copper was retained in the product. Second, when compound **2**-A was washed with acid, none of the copper was washed out (the C:Cu mole ratio remained constant at ~55:1 before and after washing). This implies that, in type A reactions where both copper and iron are present, the formation of copper phthalocyanine cores is completely dominant.

The question of whether the mixed imide–acid monomers are structurally homogeneous cannot be answered at this time. However, such complexes are not gross mixtures of all possible acid–imide combinations because the octa-acid compounds are soluble in water and would thus be separated from the complexes con-

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[13] A. B. P. Lever, *Advan. Inorg. Chem. Radiochem.*, **7**, 28, 63 (1965).

taining three or four imide groups per ring when the compounds are washed during the acid extraction.

The catalytic activity of the type A complexes requires a thorough reexamination, and such is currently under way in our laboratory.

B. Type B Complexes.—In a study by Drinkard and Bailar,[2] it was assumed that the products of reaction B were phthalocyanine derivatives containing peripheral carboxylic acid functional groups exclusively. The structures of the products were deduced by reference to an elemental analysis chart similar to that used in this work. However, metal analyses were not reported, and the infrared spectra were not examined.

Present attempts to prepare these compounds have resulted in products which have C, H, and N analyses in the ranges previously reported, and colors similar to those reported, but the copper analyses of the products are all grossly low (see Experimental Section). Furthermore, the infrared spectra and solubility behavior of the compounds do not bear out the assumption that only acid groups are present. On the contrary, the spectra very much resemble the spectrum of pyromellitimide (Figure 3), and the complete insolubility of the products in water and in organic solvents is in contrast to the ready solubility of the octa-acid type A derivatives. Our efforts to purify these compounds by solvent or acid extraction techniques were not successful; the compounds apparently contain an organic impurity which is as insoluble as the metal complex.

However, hydrolysis of the products in hot 50% KOH destroys the organic impurity and allows one to obtain water-soluble derivatives. Infrared spectra of the type B hydrolysis products show that only carboxylic acid functional groups are present, and elemental analyses of the compounds (Table V) identify them as oligomeric phthalocyanine derivatives with carboxylic acid functional groups at the peripheral sites (see Experimental Section for empirical formulas). Table VIII shows the C:N, C:M, and N:M ratios for some type B hydrolysis products. Comparison of the C:N ratios of these samples with those in Table Ia indicates that sample **1**-B is a monomer, **2**-B is a dimer, **3**-B is a tetramer, and **4**-B is a pentamer. However, the C:M and N:M ratios show that the metal content of the compounds, except for **2**-B, is low.

TABLE VIII

PERTINENT RATIOS FOR VARIOUS TYPE B HYDROLYSIS PRODUCTS

	1-B	**2**-B	**3**-B	**4**-B
C/N	4.83	4.37	3.97	4.08
C/M	42.02	32.23	38.5	40.2
N/M	8.7	7.4	9.65	12.1

The excellent agreement of the C, H, and N analyses for these complexes leads us to conclude that they are quite pure and are not mixtures of oligomers. Therefore, it is thought that the low metal content is due to "unfilled" phthalocyanine sites within the oligomeric chains, or possibly to methodological problems in the analysis of these very stable molecules.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Nuclear Magnetic Resonance Spectra of Some Oxygen-, Sulfur-, and Nitrogen-Bridged Diphosphorus Tetrafluoride Compounds

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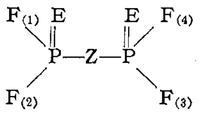
The nmr spectra of bridged tetrafluorodiphosphorus molecules of the types $F_2P(E)ZP(E)F_2$ [E = O, S; Z = O, S, NCH_3, NH] have been analyzed in terms of an XX′X″X‴AA′ spin system which allows all possible couplings to be nonzero. The coupling constants for all of the compounds at 33° are reported. The compound $(SPF_2)_2O$ shows a relatively substantial variation of the $^2J_{PP}$ coupling constant with temperature whereas $(OPF_2)_2O$ and $(PF_2)_2O$ show little or no change of this coupling with temperature. The remaining molecules show intermediate $^2J_{PP}$ variations with temperature. Signs and assignments of coupling constants are discussed.

Introduction

There has been considerable recent interest in the nmr spectra of tetrafluorodiphosphorus molecules of the general type



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(where E = O, S, or nothing and Z = O, S, NCH_3) containing either pentavalent[1] or trivalent[2,3] phosphorus and also in the mixed-valence compounds[4,5] containing phosphorus in both trivalent and pentavalent states. The symmetric molecules in the above list constitute AA′XX′X″X‴ systems, the solutions for which have been given by Lynden-Bell.[6] When $J_{XX'}$ approximates zero, reasonably good estimates of the spectral parameters can be obtained by using (*e.g.*, the initial

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[1] W. E. Hill, D. W. A. Sharp, and C. B. Colburn, *J. Chem. Phys.*, **50**, 612 (1969).

[2] R. W. Rudolph and R. A. Newmark, *J. Amer. Chem. Soc.*, **92**, 1195 (1970).

[3] J. F. Nixon, *J. Chem. Soc. A*, 1087 (1969).

[4] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **8**, 2436 (1969). An error in the conversion of ^{31}P chemical shifts to the P_4O_6 reference has led to erroneous values of this parameter quoted in Table III (p 2437) of this paper. Correct chemical shifts are as follows: $F_2P(S)SPF_2$ (−40°), P(V) +38.2, P(III) −78.0; $F_2P(O)OPF_2$ (−10°), P(V) +148, P(III) +8.0 ppm *vs.* P_4O_6. Coupling constants remain as originally quoted.[4]

[5] D. D. DesMarteau, *J. Amer. Chem. Soc.*, **91**, 621 (1969).

[6] R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961); *Mol. Phys.*, **6**, 601 (1963).