"exhaustion" region; (d) a sharp rise in band conductivity due to a significant excitation of additional carriers, either from Cu^+ or possibly from oxygen atoms.

(b) **High-Copper, Triclinic $Cu_xWO_{3+\delta}$.**—The picture here is simpler since the resistivity *vs.* $1/T$ curves for these specimens consist of two straight-line portions, without any visible evidence of the up-turning hook that signals the onset of the "exhaustion" region in the low-copper materials. The simplest model would call for two donor centers of appreciable but differing excitation energies. The low temperature portion would correspond to an activation energy of 0.10 ± 0.05 e.v., which value is to be compared to the 0.15 e.v. previously reported for $Cu_{0.77}WO_3$; the high temperature portion, to an activation energy of 0.15 ± 0.05 e.v. The number of carriers as deduced from the Hall experiments is considerably less, and the carrier mobility is smaller than in the low-copper material. The low carrier mobility—0.4 cm.^{2}/v. sec. at room temperature—is not low enough to warrant unambiguous assignment to "hopping" conduction; it more likely is due to the rather low symmetry of the host structure. The fact that by 423°K. the mobility has decreased to 0.2 cm.^{2}/v. sec. suggests that lattice scattering is still the dominant mechanism of resistivity. The effective mass of the carriers is surprisingly close to the rest mass of the electron (m^* varies from 0.3 m_0 at 298°K. to 0.8 m_0 at 423°K.), though the calculation based on thermoelectric power has to be considered as rather unreliable because the band form is probably not simply spherical.

The Hall measurements indicate at 298°K. there are about 10^{18} electron carriers/cc., which is to be compared to the 1.6×10^{22} copper atoms/cc. calculated from the stoichiometry and the density. The spin-resonance studies,[16] however, indicate there are present about 10^{22} spins/cc. with a g-factor of 2.18, strongly implying that practically all of the copper atoms are in a doubly ionized state. To account for this low number of carriers but a large number of ionized copper atoms it is necessary to assume there are fairly deep traps for removing electrons from the conduction band. If these traps are excess oxygen atoms, we need about 4×10^{21} oxygen atoms/cc. This corresponds to $Cu_{0.95}WO_{3.2}$, in substantial agreement with the oxygen excess indicated by the chemical analysis.

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Phthalocyaninoaluminum Compounds[1]

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A group of phthalocyaninoaluminum compounds has been prepared and studied in which organo- and organosiloxy groups have been bonded to the central aluminum atom. These compounds illustrate some types of groups that can replace the simple inorganic groups which ordinarily are attached to the metal. One of these compounds, $PcAlOSi(C_6H_5)_3$, contains an AlOSi backbone which is not easily hydrolyzed.[2]

The phthalocyaninoaluminum compounds are complexes in which two of the primary valencies of the coördinated aluminum atom are taken up by the dibasic, quadridentate, planar phthalocyanino ligand and the third by other groups (Cl^-, Br^-, OH^-, etc.).[3,4] Because of the nature of the phthalocyanino ligand, it is probable that the arrangement of the ligand atoms surrounding the aluminum atom is square pyramidal and that the aluminum atom lies near or in the plane formed by the nitrogen atoms (Fig. 1).

This suggests that in some cases the aluminum atom is coördinated in a square pyramidal fashion.

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(1) This paper is based on a thesis submitted by James E. Owen in partial fulfillment of the requirements for the Ph.D. degree. The work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research and the Esso Foundation, and was presented at the 138th National American Chemical Society Meeting.

(2) Pc = $C_{32}H_{16}N_8$, the phthalocyanino ring.

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

(4) M. E. Kenney, *J. Inorg. & Nuclear Chem.*, **11**, 167 (1959).

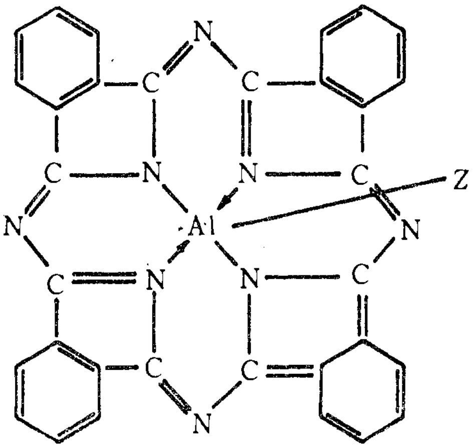

Figure 1.

However, if the vacant sixth position is filled by a Lewis base then the arrangement of the ligands around the aluminum atom is the more usual octahedral configuration. These bases may be added molecules or the apical groups or other parts of adjacent phthalocyaninoaluminum molecules.

A series of phthalocyaninoaluminum compounds now has been synthesized which is related structurally to those already reported; however, in this series the apical groups are organo- or organosiloxy groups. In the compounds isolated and identified, no added Lewis bases have been found. If the sixth position has been filled in these compounds, the atoms must have been provided by adjacent phthalocyaninoaluminum molecules. Evidence gathered on some of the intermediate reaction products suggests that the sixth position in them may have been filled by added molecules.

The final PcAlOR products were isolated and purified by high vacuum, high temperature sublimation of the initial reaction products. Studies of the chemical and physical properties of these compounds have been made.

Experimental

Hydrolyzed PcAlCl was used for the synthesis of the new derivatives. The PcAlCl was hydrolyzed with concentrated H_2SO_4 and then treated with refluxing concentrated NH_4OH and hot water and dried. The PcAlCl was prepared by the urea method.[5] Later work showed that a phthalonitrile method was convenient for the preparation of the PcAlCl. This method gave a product which was more crystalline and apparently purer, although the yield was low (approx. 35% based on phthalonitrile).

Chloro-(phthalocyanino)-aluminum (PcAlCl).—A mixture of 100 g. (0.78 mole) of phthalonitrile and 29 g. (0.22 mole) of $AlCl_3$ was added to 150 ml. of technical quinoline. The mixture was heated to 175° and held at this temperature for a period of 1.5 hr. During this heating process the reaction mixture was mechanically stirred. The mixture then was heated at reflux for 4 hr. The resulting PcAlCl was separated from the mother liquor by filtration and was washed with acetone and dimethylformamide.

Organo and Siloxy Derivatives.—These derivatives all were prepared in a similar fashion from hydrolyzed PcAlCl and the appropriate hydroxy compound. Typically at least a 10-fold mole excess of the acidic hydroxy compound was placed in 50–100 ml. of benzene together with 0.5–2.0 g. of the phthalocyanino compound ($PcAlOH \cdot H_2O$ assumed) and the resulting suspension refluxed for from 3–72 hr. Subsequently the crystalline reaction product was filtered, washed with benzene or ethanol, and dried at 125°. A sample of the initial product weighing 0.5–0.6 g. when placed in a vacuum sublimator and heated to from 350–400° yielded the final product as a crystalline sublimate. Analytical data and other pertinent observations on the individual compounds are given in the following paragraphs.

Phenoxy-(phthalocyanino)-aluminum ($PcAlOC_6H_5$).—This compound was synthesized from phenol. *Anal.* Calcd. for $C_{38}H_{21}N_8AlO$: C, 72.15; H, 3.35; N, 17.71; Al, 4.26. Found: C, 71.89; H, 3.47; N, 17.36; Al, 4.47.

The infrared spectrum of the sublimation residue showed that it was PcAlOAlPc.[6] Although the infrared spectrum of the $PcAlOC_6H_5$ resembled that of the initial reaction product, it was not identical with it. The same initial reaction product also was obtained (as determined by infrared spectra) from experiments in which the time was varied from 3–72 hr. and in which the phenol mole ratio was increased to as high as 300:1. This same initial reaction product also was obtained from experiments in which attempts were made to remove any water formed in the initial reaction by means of an azeotrope trap and by the use of $CaCl_2$.

***p*-Phenylphenoxy-(phthalocyanino)-aluminum ($PcAlOC_6H_4C_6H_5$-*p*).**—*p*-Phenylphenol was used in the preparation of this compound. *Anal.* Calcd. for $C_{44}H_{25}N_8AlO$: C, 74.57; H, 3.56; N, 15.81. Found: C, 74.82; H, 3.55; N, 16.16 As in the case of the phenoxy derivative it again was found that the spectra of the sublimate and the initial product were not the same and that the sublimation residue was PcAlOAlPc.

***p*-Methoxyphenoxy-(phthalocyanino)-aluminum ($PcAlOC_6H_4OCH_3$-*p*).**—The phenol reactant used for this compound was *p*-methoxyphenol. *Anal.* Calcd. for $C_{39}H_{23}N_8AlO_2$: C, 70.69; H, 3.50; N, 16.91. Found: C, 70.38; H, 3.58; N, 17.20. The spectrum of the residue indicated that it was neither PcAlOAlPc nor $PcAlOC_6H_4OCH_3$-*p*; perhaps it was $PcAlOC_6H_4OAlPc$-*p*.

Triphenylsiloxy-(phthalocyanino)-aluminum ($PcAlOSi(C_6H_5)_3$).—Triphenylsilanol was used for this compound. *Anal.* Calcd. for $C_{50}H_{31}N_8AlSiO$: C, 73.69; H, 3.83; N, 13.75. Found: C, 74.16; H, 3.81; N, 14.00. The spectra of the sublimate, sublimation residue, and initial reaction product were indistinguishable from one another. The spectrum of the compound showed a band at 1052 cm.$^{-1}$. A band in this position also was observed in the spectra of other phthalocyanino compounds containing the grouping AlOSi.[6]

The absorption in the spectra of all these phthalocyanino-

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[5] R. Brouillard, U. S. Patent 2,647,127 (July 28, 1953).

[6] J. E. Owen and M. E. Kenney, *Inorg. Chem.*, **1**, 334 (1962).

aluminum compounds at 903 cm.$^{-1}$ apparently is characteristic of phthalocyaninoaluminum compounds in general, other compounds in this series also having been found to exhibit it.[6]

The infrared spectra of sublimed samples of the phenoxy derivatives which had been treated with refluxing concentrated NH_4OH for 2 hr. were the same as those obtained from the samples which had been analyzed. Treatment of sublimed samples of the phenoxy compounds with refluxing 6 N H_2SO_4 for 2 hr., followed by concentrated NH_4OH and water, removed the phenoxy groups. Sublimed samples of the phenoxy compounds refluxed with water gave slightly altered spectra. However, when a sample of the $PcAlOC_6H_5$ which had been refluxed with water was resublimed, $PcAlOC_6H_5$ was recovered and no residue remained. A sample of $PcAlOSi(C_6H_5)_3$ was not decomposed by concentrated NH_4OH at reflux for 2 hr. The infrared spectrum of a sample refluxed with 12 N H_2SO_4 for 2 hr. was unaltered (although the mull appeared slightly greener). Concentrated sulfuric acid did remove the siloxy groups.

These compounds exhibited a marked stability to heat under vacuum. When the sublimed compounds were resublimed, at most only a thin green film of residue remained. In each case the infrared spectrum of the resublimed material was identical with that of the sublimed compound.

The visible spectra of the compounds dissolved in pyridine were obtained (Table II). The fact that the wave lengths at which the maxima of the absorptions occurred were constant in these spectra suggested that the group attached to the metal had little effect on the transitions corresponding to these absorptions. All of these phthalocyaninoaluminum compounds appeared blue in color when powdered, but when crystalline appeared reddish by reflected light and blue by transmitted light.

TABLE I[a]

PROMINENT INFRARED BANDS, CM.$^{-1}$

(KBr)

PcAlO-C_6H_5	PcAlO-$C_6H_4C_6H_5$-p	PcAlO-$C_6H_4OCH_3$-p	PcAlO-$Si(C_6H_5)_3$
Common bands			
735	737	737	735
761	761	761	761
903	903	903	903
1083	1083	1083	1083
1123	1123	1124	1123
Some characteristic bands			
704	705	772	704
894	841	785	1052
		797	
		835	
		880	
		1037	

[a] See ref. 7.

TABLE II[a]

VISIBLE SPECTRA

	λ_1	λ_2	λ_3
$PcAlOC_6H_5$	680	652	614
$PcAlOC_6H_4C_6H_5$-p	678	651	612
$PcAlOC_6H_4OCH_3$-p	678	649	612
$PcAlOSi(C_6H_5)_3$	679	649	612

Order of decreasing intensity: $\lambda_1 > \lambda_3 > \lambda_2$

[a] See ref. 7.

The phenoxy derivatives reacted with various substituted phenols. For example, $PcAlOC_6H_4C_6H_5$-p was isolated from the reaction of $PcAlOC_6H_5$ with p-phenylphenol in refluxing benzene. In a similar fashion $PcAlOC_6H_4OCH_3$-p reacted with p-phenylphenol in benzene at reflux to yield $PcAlOC_6H_4C_6H_5$-p.

These compounds showed solubilities ranging from low to almost zero in dimethylformamide, pyridine, ethanol, and 1-chloronaphthalene (at room temperature).

Discussion

These derivatives are significant because they have established routes for synthesizing compounds of the type PcAlOR. The reactions used to synthesize these compounds appear to be general in their scope. Substantiating this is the fact that analogous phthalocyaninogermanium and silicon derivatives have been prepared since.[8]

As an alternative to considering $PcAlOSi(C_6H_5)_3$ as a phthalocyanino derivative it can be viewed as being an organosilicon compound with a stable Al–O–Si linkage. Its structure suggests that siloxane chains with phthalocyaninoaluminum end groups are possible and further work has shown that this is the case.[6] The relationship between this compound and the completely inorganic aluminosilicates is emphasized by its relative chemical stability.

When anisole was used in place of the phenols under conditions similar to those used with the phenols a highly crystalline compound resulted. This substance when heated in a vacuum was converted principally to PcAlOAlPc, but a little was changed into $PcAlOC_6H_5$. This suggests that possibly intermediate complexes were involved in the two-step synthesis of the phenoxy derivatives. Such complexes would account for the differences between the initial and final products.

The stability of Al–N bonds in all of these compounds to chemical attack undoubtedly can be attributed to chelation. A similar stability of the Si–N and Ge–N bonds in the phthalocyaninosilicon and germanium compounds has been observed.

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(7) Reproductions of these spectra are available in the thesis of J. E. Owen, University Microfilms No. 61-3309.

(8) R. D. Joyner and M. E. Kenney, *J. Am. Chem. Soc.*, **82**, 5790 (1960); R. D. Joyner, R. G. Linck, J. Cekada, and M. E. Kenney, *J. Inorg. & Nuclear Chem.*, **15**, 387 (1960); R. D. Joyner and M. E. Kenney, *ibid.*, in press; R. D. Joyner and M. E. Kenney, *Inorg. Chem.*, **1**, 236 (1962).