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Aluminum and Silicon Hydroxy and Oxy Systems of the Phthalocyanino Type[1a]

By JAMES E. OWEN AND MALCOLM E. KENNEY

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A re-investigation of some oxy- and hydroxy-(phthalocyanino)-aluminum compounds has revealed the existence of unhydrated PcAlOH and confirmed the existence of PcAlOAlPc.[1b] Two structurally related substances also have been found which it is concluded have the formulas PcAlOSi(Pc)OAlPc and PcAlOSi(Pc)OSi(Pc)OAlPc. Hydrolysis of the second of these has yielded what appears to be HOSi(Pc)OSi(Pc)OH.

Introduction

Work on the phthalocyanino complexes by Linstead and his co-workers showed that hydrated hydroxy-(phthalocyanino)-aluminum compounds existed and that dehydration of them led to $(PcAl)_2O$. On the basis of the available evidence it was implied by these workers that this latter compound involved an oxygen linked structure, *i.e.*, PcAlOAlPc (presumably with an AlOAl type linkage).[2]

The probable existence of this type of structure indicated the possible existence of silicon subgroup phthalocyanino polymers with stable oxygen linkages between the phthalocyanino units. This situation suggested the desirability of work on oxy–metal phthalocyanino systems starting with a re-investigation of the phthalocyaninoaluminum compounds.

The outcome of this work has confirmed the earlier work on the hydroxy-oxy-(phthalocyanino)-aluminum system and in addition has led to the synthesis of oxy-linked phthalocyanino-aluminum-silicon compounds. In these, the phthalocyaninosilicon groups are sandwiched between phthalocyaninoaluminum end groups and the backbones of these compounds are accordingly of the type $AlO(SiO)_xAl$ (Fig. 1). Hydrolysis of these compounds yields phthalocyaninosilicon compounds with hydroxy end groups. These are related to the original compounds by the formal replacement of the OAlPc end groups with OH groups.

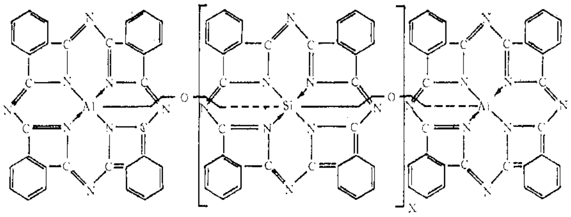

Figure 1.

The results of some work on silicon subgroup phthalocyanino polymers which was based in part on the results of the work on PcAlOAlPc reported here are given elsewhere.[3,4]

Experimental

Hydroxy-oxy-(phthalocyanino)-aluminum System.—$PcAlOH \cdot H_2O$ was obtained by hydrolyzing $PcAlBr \cdot 3py$ (py = pyridine) by treatment with excess concentrated H_2SO_4 followed by dilution, washing, refluxing with concentrated NH_4OH, and washing with hot water. It was dried at 115°. *Anal.* Calcd. for $C_{32}H_{19}N_8AlO_2$: C, 66.90; H, 3.33; N, 19.50. Found: C, 66.89; H, 3.30; N, 19.14. The compound had very low solubility in pyridine, dimethylformamide, ethanol, 1-chloronaphthalene, and dioxane. As expected, it showed a broad infrared absorption in the OH region (3375 cm.$^{-1}$).[5]

Two samples of $PcAlOH \cdot H_2O$ weighing 380.0 and 535.2 mg. were kept for 4 hr. in a closed vessel partially filled with water and then air dried for a day. The increases in weight were 26.7 and 33.8 mg., which correspond to 2.24 and 2.01 moles of water per mole of compound. On redrying at 110° the losses of weight were 26.9 and 33.5 mg.

Three samples of $PcAlOH \cdot H_2O$ amounting to 0.0200, 0.0366, and 0.0258 mmole when heated to 110° for 2 hr. in a system evacuated to 0.1 mm. yielded 0.020, 0.0364, and 0.0259 mmole of water vapor, respectively. The PcAlOH thus obtained was very hygroscopic and rapidly rehydrated when exposed to water vapor. The first two

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(1) (a) 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 139th National Meeting of the American Chemical Society; (b) Pc = $C_{32}H_{16}N_8$, the phthalocyanino ring.

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

(3) R. D. Joyner and M. E. Kenney, *J. Am. Chem. Soc.*, **82**, 5790 (1960).

(4) R. D. Joyner, Ph.D. Thesis, Case Institute of Technology, 1961; University Microfilms No. 61-3317.

(5) Reproductions of these spectra are given in the Ph.D. thesis of J. E. Owen, University Microfilms No. 61-3309.

samples when further heated yielded more water vapor (starting at about 260°). After 4 hr. at 400° the total water evolved was 0.0316 and 0.0540 mmole, respectively, indicating the loss of an additional amount of water corresponding to the formation of PcAlOAlPc.

Sublimed samples of PcAlOAlPc were prepared by heating approximately 0.8-g. samples of PcAlCl (urea process) which had been hydrolyzed (with NH_4OH and H_2O) in a vacuum sublimator at 510°. Well formed crystals of PcAlOAlPc were obtained. The infrared spectrum of these crystals was the same as that obtained from the residue and also matched the spectrum of the PcAlOAlPc produced in the water evolution experiments. *Anal.* Calcd. for $C_{64}H_{32}N_{16}Al_2O$: C, 70.20; H, 2.95; N, 20.47; Al, 4.93. Found: C, 70.46; H, 2.74; N, 20.66 (Kjeldahl), 21.26 (Dumas); Al, 4.92, 5.08. When PcAlOAlPc was resublimed only a faint green film of residue remained. It was not hygroscopic.

Sublimed samples of PcAlOAlPc were not decomposed by refluxing water, refluxing 15 *N* NaOH, and refluxing 0.1 *N* HCl. However, the AlOAl linkage was broken by concentrated H_2SO_4 at room temperature and by 6 *N* HCl at reflux.

Both $HO(Si(Pc)O)_xH$[4] and PcAlOAlPc were prepared by refluxing suspensions of the corresponding hydroxy derivatives in 1-chloronaphthalene.

Si–Al Condensation 1:2 Ratio.—In a typical synthesis 0.25 g. (0.44 mmole) of $PcSi(OH)_2$ and 0.60 g. (1.04 mmoles) of $PcAlOH \cdot H_2O$ were ground together. (Alternatively an intimate phthalocyanino mixture was prepared by dissolving the two hydroxy derivatives in concentrated H_2SO_4, diluting, and then following with treatment with concentrated NH_4OH and H_2O.) The mixture then was put in 50 ml. of 1-chloronaphthalene and refluxed for 4 hr. The resulting product was filtered off, washed with benzene, and dried for 1 hr. at 125°. Vacuum sublimation of the product from 1-chloronaphthalene at 540° yielded a band of well formed crystals of an aluminosiloxane assumed to be PcAlOSi(Pc)OAlPc (plus a small separate band of PcAlOAlPc). *Anal.* Calcd. for $C_{96}H_{48}N_{24}O_2Al_2Si$: C, 69.81; H, 2.93; N, 20.35; Al, 3.27; Si, 1.70. Found: C, 69.98; H, 2.58; N, 20.77; Al, 3.55; Si, 1.67. In view of the apparently erratic values for Si and Al obtained on samples of the other aluminosiloxane, little reliance is placed on the values obtained for the Al–Si combination.

The infrared spectrum of this substance was similar to that of PcAlOAlPc except that two absorptions appeared in the 900-cm.$^{-1}$ region, one at 903 cm.$^{-1}$ and the other at 908 cm.$^{-1}$. This indicated the presence of both Al and Si, since a band at 903 cm.$^{-1}$ has been found to be characteristic of phthalocyaninoaluminum compounds and a band at a slightly higher frequency to be indicative of phthalocyaninosilicon compounds.

Hydrolysis of a sublimed sample of this substance with concentrated H_2SO_4, concentrated NH_4OH, and water broke the AlOSiOAl backbone. Hydrolysis of a sublimed sample of it with concentrated HBr at reflux for 0.5 hr. followed by an extraction of the product with a hot pyridine–HBr solution separated the silicon and aluminum containing residues. $PcAlBr \cdot 3py$ was isolated from the pyridine–HBr solution and $PcSi(OH)_2$ from the pyridine–HBr insoluble residue after washing with acetone and concentrated NH_4OH.

Si–Al Condensation 1:1 Ratio.—In a typical preparation a finely ground mixture of 0.517 g. (0.900 mmole) of $PcAlOH \cdot H_2O$ and 0.517 g. (0.900 mmole) of $PcSi(OH)_2$ was refluxed in 1-chloronaphthalene for 4 hr. and the product filtered, washed with benzene, and dried at 125°. The compound was purified by vacuum sublimation at 540°. Low yields (<4%) of small well-formed cyrstals were obtained. The infrared spectra of the sublimate and initial product were the same. The product was assumed to be PcAlOSi(Pc)OSi(Pc)OAlPc. *Anal.* Calcd. for $C_{128}H_{64}N_{32}Al_2Si_2O_3$: C, 69.62; H, 2.92; Si, 2.54; Al, 2.44. Found: C, 69.85; H, 2.73; Si, 3.71; 2.39; Al, 1.08, 4.26. The spectrum of this substance also showed bands at 903 and 908 cm.$^{-1}$, again indicating the presence of both silicon and aluminum.

The unsublimed product was hydrolyzed with refluxing 48% HBr for 0.5 hr. and then extracted with pyridine–HBr. $PcAlBr \cdot 3py$ was obtained from the pyridine solution. The residue from the extraction was further washed and then analyzed. The final product had a composition corresponding to that of HOSi(Pc)OSi(Pc)OH. *Anal.* Calcd. for $C_{64}H_{34}N_{16}Si_2O_3$: C, 67.95; H, 3.03; Si, 4.97. Found: C, 66.72, 68.58; H, 3.27, 2.65; Si, 4.98, 6.02. In addition to other bands the infrared spectrum of this material showed absorptions at 3535, 913, and 841 cm.$^{-1}$. These are interpreted as being due to the OH, SiPc, and SiOH groupings, respectively. A broad band at 978 cm.$^{-1}$ also was found and is thought to be due to the SiOSi stretch somewhat displaced from its ordinary position because of the unusual coördination of the silicon. No adsorption was noted at or near 903 cm.$^{-1}$. When this product was heated in an apparatus evacuated to 0.1 mm., water was evolved at about 400°. Two samples of 0.0294 and 0.0518 mmole yielded 0.0286 and 0.0519 mmole of water, respectively, when heated at 415°, corresponding to the formation of $HO(Si(Pc)O)_xH$. The spectrum of the product matched the spectrum of a known sample of $HO(SiPcO)_xH$.[4] *Anal.* Calcd. for $C_{32}H_{16}N_8SiO$: C, 69.05; H, 2.90; N, 20.13; Si, 5.06. Found: C, 70.25, 69.64, 69.83; H, 2.45, 2.99, 2.94; N, 19.15; Si, 4.98.

The compound assumed to be $HO(Si(Pc)O)_2H$ was found to be soluble in benzyl alcohol (presumably with reaction to form a compound in which benzyloxy groups replaced the hydroxy groups).

The spectra of the phthalocyaninoaluminum compounds prepared in this work containing either an AlOAl or AlOSi grouping showed similarly shaped, though presently unassigned, absorptions at 1052 cm.$^{-1}$.

TABLE I

PROMINENT INFRARED BANDS, CM.$^{-1}$[5]

$PcAlOH \cdot H_2O$	PcAlO-AlPc	PcAlOSi-(Pc)OAlPc	PcAlO-$(Si(Pc)O)_2$-AlPc	HO(Si-$(Pc)O)_2H$
		Common bands		
728	728	725	725	733
762	759	761	760	762
903	903	903	903	913
1075	1080	1081	1081	1080
1119	1120	1120	1120	1120
		Characteristic bands		
1138	1052	908	908	841
		1052	1052	978

Discussion

This series of oxy-linked compounds together with the organo series reported elsewhere[6] clearly shows the variety of groups that can be oxy-linked to the central aluminum atom in the phthalocyaninoaluminum compounds.

On the basis of other experience it might be expected that the materials obtained in the silicon–aluminum work were mixtures. However, the data gathered suggest that the AlOSi species obtained were essentially pure PcAlOSi(Pc)OAlPc (I) and PcAlOSi(Pc)OSi(Pc)OAlPc (II). While the analytical data are of little help in deciding this point, the rapidly decreasing ease of sublimation in the series of compounds identified as PcAlOAlPc, I, and II fits with their rapidly increasing calculated molecular weights (1095, 1652, and 2208) and points to little contamination in the sublimed samples with longer chain species. In the sublimation of II only a faint trace of sublimate appeared at 510°, indicating the absence of much PcAlOAlPc and, by inference, the lack of much material containing many phthalocyanino rings per molecule since the starting materials were used in a 1:1 mole ratio. Similarly the hydrolytic data indicate relatively pure species. The silicon hydrolytic product of sublimed I yielded an infrared spectrum matching that of a known sample of $PcSi(OH)_2$[4] and differing from that of the silicon hydrolytic product of II. The silicon hydrolytic product of unsublimed II gave a previously unobserved infrared spectrum. When the silicon hydrolytic product of II was heated, it gave off only half the amount of water required by $PcSi(OH)_2$ but the correct amount for HOSi(Pc)OSi(Pc)OH. On the basis of these observations it is concluded that sublimed I and unsublimed II were relatively pure species.

Compounds I and II are directly related to $HO(Si(Pc)O)_xH$ and, in fact, may be considered to be hexacoördinated siloxanes with phthalocyaninoalumino end groups. This view immediately suggests that possibly a series of phthalocyaninoalumino end-stoppered phthalocyaninopolysiloxanes of varying chain length can be prepared by methods related to those already used. The preparation of such controlled chain length aluminosiloxanes could in turn lead to the synthesis of siloxanes terminated by other end groups.

The fact that I and II can be made in good yields from mixtures of the $PcSi(OH)_2$ and $PcAlOH \cdot H_2O$ even though $PcSi(OH)_2$ under similar conditions yields $HO(Si(Pc)O)_xH$ shows that with the proper conditions the formation of the hetero backbone is favored. Perhaps the reaction yielding the AlOSi grouping is an acid–base type reaction with the $PcAlOH \cdot H_2O$ molecules yielding the hydroxyl groups and the $PcSi(OH)_2$ molecules the protons.

The rupture by acid of the AlOAl bonds in PcAlOAlPc and of the AlOSi but not the SiOSi bonds in I and II probably is related to the fact that the silicon atoms are hexacoördinate but the aluminum atoms apparently are pentacoördinate. Accordingly, the aluminum atoms are open to attack in the position *trans* to the oxygen linkages while the silicon atoms are not susceptible to a similar approach. These concepts are in agreement with the experimental observation that apparently even concentrated sulfuric acid does not decompose $HO(Si(Pc)O)_xH$.

In the usual hexacoördinate metal phthalocyanines the *trans* groups are identical but in II the groups bonded in *trans* positions on the silicon atoms are different. HOSi(Pc)OSi(Pc)OH also offers an illustration of this structural feature.

Finally, it should be pointed out that I and II may be considered to be related to PcAlOAlPc by the replacement of the single oxygen atom linkages of PcAlOAlPc by longer linkages. A somewhat analogous case in which long linkages separate germanium phthalocyanino units has been reported.[7]

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(6) J. E. Owen and M. E. Kenney, *Inorg. Chem.*, **1**, 331 (1962).

(7) R. D. Joyner, R. G. Linck, J. N. Esposito, and M. E. Kenney, *J. Inorg. & Nuclear Chem.*, in press.