

lower chloride concentration alone, and the apparent concentration equilibrium constant for chloride association would have been decreased. The following values of  $K_1$  were found for the  $\text{Pt}(\text{en})_3^{+4}-\text{Cl}^-$  ion-pair at  $I = 0.5$ . At  $[\text{Cl}^-] = 0.5$ ,  $K_1 = 0.60$ ;  $[\text{Cl}^-] = 0.4$ ,  $K_1 = 0.66$ ; at  $[\text{Cl}^-] = 0.30$ ,  $K_1 = 0.68$ ;  $[\text{Cl}^-] = 0.2$ ,  $K_1 = 0.73$ ; and at  $[\text{Cl}^-] = 0.1$ ,  $K_1 = 0.75$ . This trend is in the opposite direction to that required by the presence of perchlorate complexes and so seems to rule out their formation in this system. The shift in  $K_1$  values actually observed undoubtedly reflects changes in activity coefficients despite constant ionic strength.

### Discussion

The values found for  $K_1^0$  for the association  $\text{Pt}(\text{en})_3^{+4}$  with  $\text{Cl}^-$  and  $\text{Br}^-$  indicate that the corresponding values for +3 cations are quite small. Thus, as the work of King, Espensen and Visco has shown, earlier studies tended to overestimate by orders of magnitude the importance of such association in solutions of cobalt amines. The  $K_1^0$  values here determined, 11 for  $\text{Cl}^-$  and 8 for  $\text{Br}^-$  association, reflect the identical charge of the two

anions and the fact that  $\text{Cl}^-$  is but slightly smaller than  $\text{Br}^-$ .

The oxyanions studied provide an interesting series for comparison. Although the very large association of  $\text{SO}_4^{2-}$  can be understood in terms of its greater over-all charge, the difference between  $\text{NO}_3^-$  and  $\text{ClO}_4^-$  is not so obvious. Since the association of  $\text{NO}_3^-$  is most probably through an O as opposed to the N, the fact that it is a planar ion should matter little. However, the difference is reasonable in terms of the charge density at the O atoms in the two cases. Recent studies of absolute Raman intensities have indicated the relative extent of  $\pi$  bonding in oxyanions from which approximate partial charges can be assigned to the O atoms in each of the anions studied.<sup>11</sup> These are  $-3/4$  for  $\text{SO}_4^{2-}$ ,  $-2/3$  for  $\text{NO}_3^-$  and  $-1/2$  for  $\text{ClO}_4^-$ . Thus, the relative tendency toward decreased outer-sphere association follows the order of decreasing charge density at the oxygen atom. It should be noted, however, that an argument of this sort is useful only in comparing similar anions, since the larger value found for  $\text{SO}_4^{2-}$  than for  $\text{Cl}^-$  indicates the importance of the over-all charge of the ion.

(11) G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **32**, 319 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT CASE INSTITUTE OF TECHNOLOGY, UNIVERSITY CIRCLE, CLEVELAND, OHIO]

## Germanium Phthalocyanines<sup>1</sup>

BY RALPH D. JOYNER AND MALCOLM E. KENNEY

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Work on new stable germanium phthalocyanines is reported in which advantage is taken of the inorganic functionality of these phthalocyanines and use is made of the hexacoordination possessed by the germanium. The compounds discussed include a chloride, a hydroxide, two phenoxides and a siloxide. These compounds point to a variety of possible germanium substituted phthalocyanines with widely varying properties and illustrate some of the behavior of germanium when it is hexacoordinated to four nitrogen plus two chlorine or oxygen atoms.

Tin and lead phthalocyanines have been known for some time; but specific germanium phthalocyanines have not been described in the literature, although some work on them has been reported by Colaitis.<sup>2</sup> The germanium phthalocyanines are important not only because few metal phthalocyanines are known in which the central element has as large an electronegativity as germanium but also because they provide an opportunity for the study of germanium when it is bound to six atoms, of which four are nitrogens that can be assumed to be in a planar arrangement.<sup>3</sup> Due to the great stability of the phthalocyanine ring system, this unusual partly predetermined hexacoordination for germanium is preserved under a wide variety of conditions.

The germanium phthalocyanines are notable also in that they exhibit a functionality associated with the two non-ring atoms bonded to the germanium—a kind of functionality which is seldom fully utilized in phthalocyanine chemistry. The use of this inor-

ganic functionality in synthesizing a series of metal substituted germanium phthalocyanines, and the exploitation of the stable phthalocyanine ring for controlling the number and positions of atoms surrounding the germanium are described in the accompanying experimental work.

### Experimental

**Dichlorogermanium Phthalocyanine.**—A mixture of 20 g. (0.094 mole) of germanium tetrachloride and 50 g. (0.39 mole) of phthalocyanine was placed in 100 ml. of quinoline and brought very slowly to reflux with constant stirring. Heating and stirring were continued at 240° for 4 hr. The reaction mixture was filtered hot and the solid product extracted in a Soxhlet extractor with successive portions of dimethylformamide, xylene and acetone. The yield was approximately 50% based on germanium tetrachloride. Repeated attempts at recrystallization failed because of the low solubility of the dichloride.

Purification was effected by heating a 300 mg. sample, covered with platinum gauze, in a vacuum sublimator at 450–460° for 2 hr. under a pressure of 2 microns. The collecting finger of the sublimator was maintained at 357° by mercury held at reflux with an independent heat source. A yield of 75 mg. of crystals which under microscopic examination were uniform in size, shape and color was obtained. The crystals were blue-green by transmitted light and had a reddish reflex. Germanium was determined by conversion to the oxide.

(1) This research was supported in part by a grant from the Research Corporation of America.

(2) D. Colaitis, *Compt. rend.*, **242**, 1026 (1956).

(3) R. P. Linstead and J. M. Robertson, *J. Chem. Soc.*, 1736 (1936).

*Anal.* Calcd. for  $C_{32}H_{16}N_8GeCl_2$ : C, 58.59; H, 2.46; Ge, 11.07; Cl, 10.81. Found: C, 58.70; H, 2.67; Ge, 11.1; Cl, 10.65.

**Dihydroxygermanium Phthalocyanine.**—Hydrolysis of the dichloride was slow with water, refluxing concentrated ammonia, live steam and refluxing pyridine. However, a 300 mg. sample of the sublimed dichloride was hydrolyzed completely with 20 ml. of refluxing 1:1 pyridine-concentrated ammonia solution in 6 hr. The blue hydroxide was not hygroscopic and dried completely at 110°.

*Anal.* Calcd. for  $C_{32}H_{18}N_8GeO_2$ : C, 62.17; H, 2.94; N, 18.13. Found: C, 62.88; H, 2.96; N, 17.74.

Treatment of the dichloride with concentrated sulfuric acid gave, after dilution and washing, dihydroxygermanium phthalocyanine, which was apparently uncontaminated with metal free phthalocyanine.

**Diphenoxygermanium Phthalocyanine.**—Reaction of 1.0 g. (0.0016 mole) of dihydroxygermanium phthalocyanine and 1.5 g. (0.016 mole) of phenol in 50 ml. of refluxing benzene for 3 hr. produced crystalline diphenoxygermanium phthalocyanine in very high yield. A 400 mg. sample of this product was heated at 385° for 2.5 hr. under a pressure of 2 microns in a sublimator equipped with an air cooled cold finger. A band of 17 mg. of uniform air stable crystals which were blue-green by transmitted light and reddish by reflected light was obtained.

*Anal.* Calcd. for  $C_{44}H_{26}N_8GeO_2$ : C, 68.51; H, 3.40; N, 14.53; Ge, 9.41. Found: C, 68.37; H, 3.46; N, 14.63; Ge, 9.18.

**Bis-(*p*-phenylphenoxy)-germanium Phthalocyanine.**—A mixture of 2.8 g. (0.016 mole) of *p*-phenylphenol and 1.0 g. (0.0016 mole) of the dihydroxide in 50 ml. of refluxing benzene gave a high yield of crystalline bis-(*p*-phenylphenoxy)-germanium phthalocyanine after 3 hr. A 300 mg. sample heated at 355° for 3.5 hr. at a vacuum of 2 microns yielded a ring of 17 mg. of uniform air stable crystals blue-green by transmitted and reddish by reflected light.

*Anal.* Calcd. for  $C_{56}H_{34}N_8GeO_2$ : C, 72.83; H, 3.71; N, 12.13. Found: C, 72.93; H, 3.96; N, 11.77.

**Bis-(triphenylsiloxy)-germanium Phthalocyanine.**—A mixture of 4.5 g. (0.016 mole) of triphenylsilanol and 1.0 g. (0.0016 mole) of the dihydroxide reacted in refluxing benzene in 3 hr. to give an almost quantitative yield of bis-(triphenylsiloxy)-germanium phthalocyanine. A 500 mg. sample of it heated at 390° for 2 hr. at a pressure of 2 microns gave 20 mg. of homogeneous air stable crystals which were blue-green by transmitted and reddish by reflected light.

*Anal.* Calcd. for  $C_{68}H_{46}N_8GeSi_2O_2$ : C, 72.16; H, 4.08; N, 9.87. Found: C, 71.52; H, 4.08; N, 9.71.

### Discussion

In dichlorogermanium phthalocyanine the germanium is surrounded by two chlorine and four nitrogen atoms in what may be assumed to be octahedral fashion. This somewhat unusual hexaco-

ordination and the size of the organic residue correlate well with the relative difficulty of hydrolysis of the dichloride (live steam gives complete hydrolysis only after 14 hr).

The replacement of the two chlorine atoms of dichlorogermanium phthalocyanine with simple or complex groups (H,  $C_6H_5$  etc.) attached to the germanium by oxygen bridges is significant because these groups represent a type of metal phthalocyanine functionality not often fully used and because they demonstrate the varied and complex nature of the residues which can be metal-bonded to phthalocyanines by this functionality.

The infrared spectrum of each of the compounds is characteristic and cannot in any case be ascribed to a mere mixture of reactants. Absorptions very near 700  $cm^{-1}$  are found in the spectra of the phenoxy (700  $cm^{-1}$ ), *p*-phenylphenoxy (705  $cm^{-1}$ ) and siloxy compounds (702  $cm^{-1}$ ). These absorptions may be attributed to the monosubstituted benzenes. The nearest absorption for the dichloride is at 690  $cm^{-1}$  while the dihydroxide has none in the immediate neighborhood. Since all of the compounds show absorptions at 770–730  $cm^{-1}$ , this region cannot be used to further confirm the presence of monosubstituted benzene rings. Only two of the compounds have peaks in the 1270–1230  $cm^{-1}$  area (1260  $cm^{-1}$  for the phenoxy and 1250  $cm^{-1}$  for the *p*-phenylphenoxy derivative). Possibly these absorptions may be due to the CO link.<sup>4</sup> The dihydroxide, dichloride, *p*-phenyl phenoxy and siloxide all show some absorption in the aromatic CH stretching region; however, in keeping with the low percentage of hydrogen this absorption is not particularly strong. The dihydroxide shows a strong peak at 3500  $cm^{-1}$  which is undoubtedly due to OH stretching. When the dihydroxide is heated it does not volatilize, but it does change color slightly. In the spectrum of this new material the 3500  $cm^{-1}$  peak is absent suggesting the formation of an oxygen bridged polymer ( $C_{32}H_{16}N_8GeO$ )<sub>x</sub>.

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(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 114.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID COMPANY, STAMFORD, CONNECTICUT]

## The Basicity of Phosphines

BY WM. A. HENDERSON, JR., AND C. A. STREULI

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Equations have been derived which allow the prediction of the base strength of phosphines. The basicity of phosphines has been correlated with inductive, resonance, steric and hybridization effects. Important differences between the basicities of amines and phosphines are pointed out.

There is in the literature no comprehensive correlation of the structure of phosphines and their basicity toward a proton. Davies and Addis<sup>1</sup> determined the  $pK_a$ 's of six methyl-substituted phenyldiethylphosphines in 50% ethanol and

(1) W. C. Davies and H. W. Addis, *J. Chem. Soc.*, 1622 (1937).

came to the conclusion that the steric effect of ortho-substituents is of lesser importance than the inductive effect. Brown<sup>2</sup> commented on the qualitative basicity series  $Me_3P > Me_2PH > MePH_2 > PH_3$  and concluded that unlike the case for

(2) H. C. Brown, *THIS JOURNAL*, **67**, 503 (1945).