bands of a complex shift toward lower wave numbers, when Cl^- coördinated on a metal atom is replaced by Br^- and also when Br^- is substituted with I^-. This rule seems to hold[40] also for the present compounds. Accordingly, the energy separation between d_π and anti-bonding d_σ levels decreases with decreasing ionic character in the order of hexachloroplatinate(IV), hexabromoplatinate(IV) and hexaiodoplatinate(IV). Conceivable causes for the energy separation are electrostatic effect and covalent bonding effect, the effect of π-bonding being disregarded. One is tempted to presume from the parallelism between the energy separation and the ionic character that the electrostatic effect is mainly responsible for the energy separation. However, this presumption can be made only with reservations, since the parallelism shows only the balance between the changes in the electrostatic effect and the covalent bonding effect accompanying the replacement of halogen ions with heavier ones.

[40] C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 518 (1956).

[Contribution from the Department of Chemistry, Cornell University, Ithaca, New York]

The Association of Trisethylenediamineplatinum(IV) with Various Anions[1a]

By C. J. Nyman[1b] and R. A. Plane

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From measurements of absorption spectra in the region 255 to 270 mμ the extent of association of $Pt(en)_3^{+4}$ with Cl^-, Br^-, $SO_4^=$, NO_3^- and ClO_4^- were determined. Of these anions all but the last were found to form a 1 to 1 outer-sphere ion-pair. An extended Debye–Hückel activity coefficient equation was used to determine values of association constants at infinite dilution. The values thus found were 11 for Cl^-, 8 for Br^-, 3.3×10^3 for $SO_4^=$ and ca. 0.8 for NO_3^-. The lack of increased absorption when ClO_4^- is added to solutions of $Pt(en)_3^{+4}$ and the fact that ClO_4^- does not lower the association of Cl^- with $Pt(en)_3^{+4}$ at constant ionic strength are taken to indicate that the association of even a +4 complex cation with ClO_4^- is negligible.

In recent years a number of articles have appeared on the stability of outer-sphere complexes formed by complex metal cations with various anions. The results of these investigations have been summarized by Basolo and Pearson[1c] and include some widely quoted values of Evans and Nancollas.[2] These later authors have reported sets of stability constants and thermodynamic properties for complexes of $Co(NH_3)_6^{+3}$ and $Co(en)_3^{+3}$ with various anions. Recently, King, Espensen and Visco[3] have shown that the stability constant for the $Co(NH_3)_6^{+3}$–Cl^- ion pair is actually much smaller than the value 74 reported by Evans and Nancollas that the proper value of K_1^0 was less than 5. Although King and co-workers were able to set an upper limit on the constant, they could not set a lower limit. In view of this discrepancy, the present work was undertaken to establish the magnitude of the association constants for outer-sphere complexes of complex cations and also to determine the effect of size and charge of the anion on the magnitude of the stability constant of the ion pairs. The trisethylenediamineplatinum(IV), $Pt(en)_3^{+4}$, cation was chosen because complexes of this cation should be somewhat more stable than those of cobalt(III) by reason of its higher charge. Thus ion-pairs would be easier to detect at the low concentrations of complexing anion corresponding to low ionic strengths, and hence activity coefficient problems should be minimal. Furthermore, the high-charge of the cation increases the possibility of finding a case of ClO_4^- association.

Experimental

Chemicals.—$[Pt(en)_3]Cl_4$ was prepared starting with scrap platinum which was purified by the barium carbonate procedure of Wichers.[4] The Pt thus purified was converted to H_2PtCl_6 by dissolution in aqua regia, and the nitric acid removed by three evaporations almost to dryness with concentrated hydrochloric acid. Platinum then was precipitated as $(NH_4)_2PtCl_6$ and converted back to the metal by thermal decomposition. This process was repeated three times to insure purity.[5] The last preparation of $H_2PtCl_6 \cdot xH_2O$ was dissolved in absolute ethanol and converted to $[Pt(en)_3]Cl_4$.[6] Excess of 98% ethylenediamine was added dropwise to the cold solution with stirring, and subsequently the mixture was heated to 75° for one hour also with constant stirring. The crude product was recrystallized several times by the following procedure. Ten grams of crude $[Pt(en)_3]Cl_4$ was dissolved in 20 ml. of water at the boiling point; 20 ml. of concentrated hydrochloric acid was added and a precipitate immediately formed. Sufficient water (approximately 80 ml.) then was added until the precipitate just redissolved completely. The sample was filtered rapidly and allowed to stand for several hours so that slow crystallization occurred. The colorless product was collected on a Hirsch funnel and washed twice with 10 ml. portions of cold 1:1 HCl to H_2O, and finally with a minimum amount of cold water. After drying for 3 hours at 125° in an oven, 8.8 g. of purified product was obtained.

After a second recrystallization, a typical analysis and that of the sample used in the investigation was: Pt: Found, 37.67%. Theoretical for $[Pt(en)_3]Cl_4$, 37.73%. Cl: Found, 27.43%. Theoretical for $[Pt(en)_3]Cl_4$, 27.41%.

$NaClO_4$ was prepared by the neutralization of reagent grade NaOH and $HClO_4$ solutions and crystallizing. The other sodium salts (which were dried at 110°) and the acids were reagent grade, used without further purification.

Water employed in the spectrophotometric studies was redistilled from alkaline permanganate in a Barnstead still, and was of the quality of "Conductivity Water."

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[1] (a) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-279. Reproduction in whole or in part is permitted for any purpose of the United States Government. (b) On sabbatical leave from the Department of Chemistry, Washington State University. (c) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, New York, 1958, p. 380.

[2] M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953).

[3] E. L. King, J. H. Espensen and R. E. Visco, *J. Phys. Chem.*, **63**, 755 (1959).

[4] E. Wichers, This Journal, **46**, 1818 (1924).

[5] E. Wichers, *ibid.*, **43**, 1268 (1921).

[6] A. P. Smirnoff, *Helv. Chim. Acta*, **3**, 177 (1920); F. Basolo, J. C. Bailar, Jr., and Betty Rapp Tarr, This Journal, **72**, 2438 (1950); and J. R. Hall and R. A. Plowman, *Australian J. Chem.*, **8**, 158 (1955).

Solutions.—Stock solutions of the various salts were prepared by diluting weighed amounts to volume, and the necessary more dilute stock solutions of complexing anions were prepared by appropriate second dilutions. Perchloric and sulfuric acids were prepared and standardized by usual procedures.

Chloride-free solutions of $[Pt(en)_3](ClO_4)_4$ were prepared by treating a solution of the chloride with the stoichiometric quantity of silver perchlorate. After standing to allow coagulation of the silver chloride, the solid was collected on a filter, washed, and the solution and washings were diluted to volume.

Samples whose absorbancy were to be determined were prepared by pipetting stock solutions into 10 ml. flasks and diluting to volume. All solutions contained 1.002, 1.020 or 1.029×10^{-3} *M* $Pt(en)_3^{+4}$, 1×10^{-3} *M* H^+, 5.1×10^{-3}*M* Cl^- or ClO_4^- plus the sodium salt of the complexing anions. For the addition of sulfate a stock solution of 1.056 *M* Na_2SO_4 plus 5.03×10^{-2} *M* H_2SO_4 (or a diluted sample of it) was employed in place of the sodium salt alone. This allowed the *p*H to be maintained at 3 or less in the final solutions in order to suppress acid dissociation of the $Pt(en)_3^{+4}$.

Procedure.—A Beckman Model DU Spectrophotometer was employed to determine the absorbancy of the solutions using a hydrogen lamp and 1 cm. matched quartz cells. A slit width of 0.7 mm. was employed for all studies except the nitrate system where wider slit widths were required because of the absorbancy of the nitrate ion itself. The absorbancy was measured against water for all systems except NO_3^-. For Cl^-, ClO_4^- and $SO_4^=$ no blank correction was necessary, but for the bromide system a slight correction was required because of the absorption due to bromide ion. Nitrate ion has a very distinctive absorption band in the region being studied, and the reference solutions in this instance were sodium nitrate of the same concentration as in the solution being investigated. All solutions were maintained at a temperature of (25 ± 0.2)° during measurement by using Beckman thermospacers in conjunction with a constant temperature water bath.

Evaluation of Thermodynamic Association Constants (K_1^0).—It can be shown[7] that the equation

$$\frac{1}{K_1^0(e_1 - e_0)} = \frac{(b - x)}{(D - e_0)}\frac{f_+f_-}{f_{ip}} - \frac{(b - x)}{(e_1 - e_0)}\frac{f_+f_-}{f_{ip}} \quad (1)$$

describes the relationship between K_1^0, the thermodynamic association constant, e_1 and e_0, the molar extinction coefficients of the 1:1 outer-sphere ion pair and the $Pt(en)_3^{+4}$ cation, respectively, *b*, the total concentration of the associating anion, *x*, the equilibrium concentration of the ion, and f_+, f_- and f_{ip}, the activity coefficients of the $Pt(en)_3^{+4}$ cation, the associating anion and the ion-pair, respectively. *D* is the apparent molar extinction coefficient, equal to the optical density per cm. per molar concentration of total platinum.

K_1^0 can be evaluated from equation (1) either by the successive approximation method of Bale, Davies and Monk,[7] or graphically. In the latter procedure, the commonly employed "slope-intercept" method, measured values of *D* are used to evaluate the first term on the right of equation 1, which is plotted *versus* $(b - x)\ f_+f_-/f_{ip}$. In either case, it is necessary to evaluate the activity coefficient ratio. This is done conveniently by using the Davies form of the modified Debye–Hückel equation.[8]

$$-\log f_i = 0.5Z_i^2\{I^{1/2}/(1 + I^{1/2}) - CI\} \quad (2)$$

where *C* is an arbitrary constant, Z_i is the charge on the ion, and *I* is the ionic strength of the solution.

Values of the ratio f_+f_-/f_{ip} for use in the above analysis are calculated using a trial value of $C = 0.2$ as suggested by Bale, Davies and Monk.[7] Successive trials with changed values of *C* can be made to decide which value produces the most constant K_1^0. However, in the low ionic strengths used in the present study, the first term of equation 2 dominates so strongly that K_1^0 changes but slightly as *C* is varied.

From the equilibrium constant and the fact that *x* is equal to $a\,(D - e_0)/(e_1 - e_0)$ where *a* is the total concentration of complex cation, an equation for *D* can be written as

$$D = e_0 + K_1^0(e_1 - e_0)\,b\left(\frac{f_+f_-}{f_{ip}}\right) + \left[\frac{(x^2 - (a + b)x)}{a}\,K_1^0(e_1 - e_0)\left(\frac{f_+f_-}{f_{ip}}\right)\right] \quad (3)$$

For a similar case, it has been shown[9] that in the limit of slight ion pairing, equation 3 reduces to

$$D = e_0 + mbf_+f_-/f_{ip} \quad (4)$$

where *m* is a constant equal to the slope. A plot of *D versus* bf_+f_-/f_{ip} should be a straight line at low ligand concentrations for 1:1 complexes with an intercept equal to e_0.

Results

The data obtained at 255 mμ for complexes of $Pt(en)_3^{+4}$ with four different anions are represented graphically in Figure 1 by a plot of *D versus* $b.f_+f_-/f_{ip}$. Similar results were obtained at other wave lengths. The activity coefficient ratios were calculated using equation 2 to obtain the individual ion coefficients taking $C = 0.2$ for the Cl^-, Br^- and NO_3^- systems, and $C = 0.6$ for the $SO_4^=$ system. These plots indicate that at low ligand concentrations the complex species is a 1:1 entity or the ion-pair.

In Table I are presented typical data from the study of chloride complexes of $Pt(en)_3^{+4}$. Only alternate points are included in the table, but all points were considered in determining the constant listed in Table II. This table contains equilibrium constants for all anions studied.

TABLE I

OPTICAL DENSITY OF SOLUTIONS OF $Pt(en)_3^{+4}$ AND Cl^- AT 25°

$Pt(en)_3^{+4} = 1.02 \times 10^{-3}$ mole/l.; $H^+ = 1.02 \times 10^{-3}$ mole/l.

[Cl] mole/l.	Apparent molar extinction coefficient ($O.D./[Pt]_{total}$). 270 mμ	265 mμ	260 mμ	255 mμ	K_1 at 255 mμ	K_1^0
0.00	139	195	260	344	..	..
5.1×10^{-3}	149	210	282	379	4.76	11.3
7.1×10^{-3}	151	213	288	388	4.33	11.0
1.21×10^{-2}	159	224	305	412	3.99	11.6
1.51×10^{-2}	160	227	311	421	3.64	11.3
3.51×10^{-2}	175	249	341	466	2.55	11.2
7.51×10^{-2}	185	266	367	509	1.67	11.1
1.05×10^{-1}	192	275	382	532	1.39	11.3
3.05×10^{-1}	217	316	443	623	0.761	11.6
5.05×10^{-1}	236	344	489	689	0.60	10.9
7.05×10^{-1}	257	373	529	743	0.53	9.6

The values of e_0 in Table I were obtained as the intercept on extrapolation of plots of the type in Figure 1 to $bf_+f_-/f_{ip} = 0$. The values of e_0 ob-

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(7) W. D. Bale, E. W. Davies and C. B. Monk, *Trans. Faraday Soc.* **52**, 816 (1956).

(8) C. W. Davies, *J. Chem. Soc.*, 2093 (1938); see also, E. A. Guggenheim, *Phil. Mag.*, Series 7, **19**, 588 (1935); E. A. Guggenheim and J. C. Turgeon, *Trans. Faraday Soc.*, **51**, 747 (1955).

(9) S. R. Cohen and R. A. Plane, *J. Phys. Chem.*, **61**, 1096 (1957).

TABLE II

EQUILIBRIUM CONSTANTS FOR ASSOCIATION OF $Pt(en)_3^{+4}$ WITH VARIOUS ANIONS AND EXTINCTION COEFFICIENTS FOR THE 1:1 COMPLEX IN SOLUTIONS CONTAINING $1 \times 10^{-3} M$ H^+ AT 25°

λ	270 mμ		265 mμ		260 mμ		255 mμ		K_1^0
ion	e_1	K_1^0	e_1	K_1^0	e_1	K_1^0	e_1	K_1^0	(average)
Cl^-	472	14	876	11	1488	9	1825	11	11
$SO_4^=$	233	3.1×10^3	342	3.4×10^3	495	3.3×10^3	692	3.5×10^3	3.3×10^3
Br^{-a}	3779	8	4735	8	5260	8	5474	10	8
NO_3^-	..	1	2695	0.9	4700	0.7	6224	0.8	*ca.* 0.8
ClO_4^-	..	0	..	0	..	0	..	0	0

[a] Br^- at $\lambda = 275$ mμ; $e_1 = 3375$, $K_1^0 = 7$; Br^- at $\lambda = 280$ mμ; $e_1 = 2530$, $K_1^0 = 7$.

tained agreed within experimental error with those determined from solutions having only perchlorate as the anion.

The concentration equilibrium constant, K_1, was estimated for each individual point. By trial and error, it was found that the most constant value of K_1^0 over the widest range of concentration was obtained with f_+f_-/f_{ip} calculated with $C = 0.2$. No points were included above 0.7 M sodium chloride because no satisfactory method of handling activity coefficients exists.

It also became apparent that the values of K_1^0 obtained by the "slope-intercept" method agreed closely with those calculated for the individual points, and thus for both bromide and nitrate complexes, the values of K_1^0 reported in Table II were obtained graphically, again using $C = 0.2$ in estimating activity coefficients. Due to the small association of nitrate and the absorption of nitrate ion itself, the uncertainty is greater than for the other cases. The probable error can be judged from the scatter of the values in Table II for all complexes except nitrate where the uncertainty may be as high as ± 0.6.

For $SO_4^=$ complexes, the first approximation of b, *i.e.*, free $[SO_4^=]$, was made knowing total sulfate and observed pH, in conjunction with literature values for K_a for HSO_4^-.[10] The procedure outlined above was carried out for estimating K_1 for individual points by a series of approximations, and K_1^0 was most constant with $C = 0.6$. Bale, Davies and Monk[7] in their treatment of the $[Co(NH_3)_6]^{+3}$-$SO_4^=$ ion pair found that values of $C = 0.4$ to 0.5 were required to give a constant value of K_1^0. Since the cation here is more highly charged, it is not surprising that a larger value of C was required. The final average value of K_1^0 at 255 mμ obtained from individual points was 3.5×10^3, and the same value was obtained from the graphical slope-intercept method. The values obtained from the other three wave lengths were determined only by the graphical method.

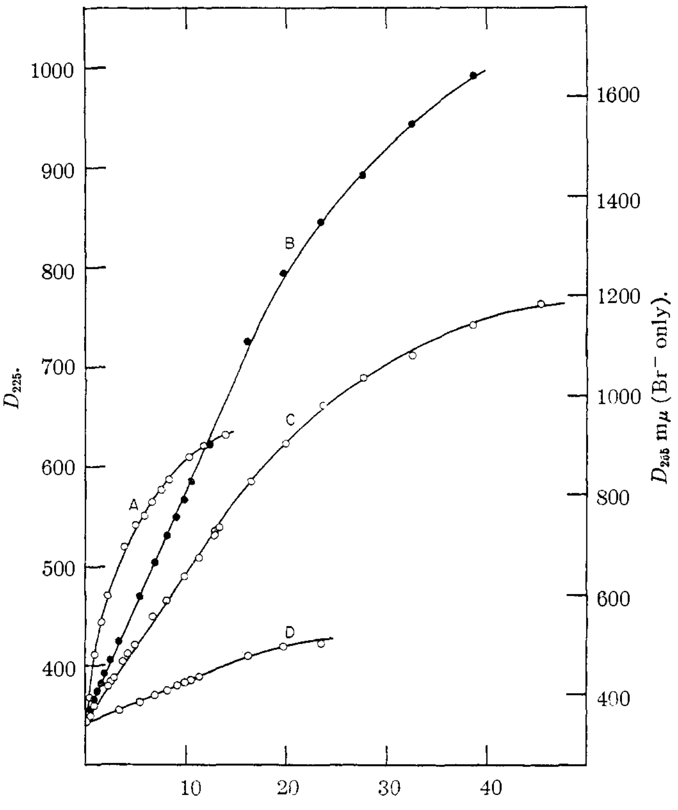

Fig. 1.—Change of optical density of $Pt(en)_3^{+4}$ at 255 mμ with anion concentration: curve A, $SO_4^=$; B, Br^-; C, Cl^-; D, NO_3^-. For curve B, use right-hand vertical scale.

Spectral measurements made of the complex with added ClO_4^- showed that either no ion-pair formation occurred between the two or that if it did there was no associated spectral change. The evidence for this was the fact that the apparent molar extinction coefficient of 1×10^{-3} M $Pt(en)_3^{+4}$ at pH = 3 was the same in 5×10^{-3} M ClO_4^- as in 0.504 M ClO_4^-. To determine whether there was ion-pair formation without spectral change, the following series of experiments were carried out. The apparent molar extinction coefficients of solutions of 1×10^{-3} M $Pt(en)_3^{+4}$, 1×10^{-3} M H^+ and various mixtures of chloride and perchlorate at $I = 0.5$ were determined. It was assumed that any spectral changes which occurred in these solutions were due to changes in the concentrations of the $Pt(en)_3^{+4}$-Cl^- ion pair. From the observed molar extinction coefficients and the previously determined values of e_1 for the $Pt(en)_3^{+3}$-Cl^- ion-pair, the concentration equilibrium constant was determined for the chloride association. If in any given solution competing perchlorate complexes were formed, the extinction coefficient should have been lowered beyond that required by the

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(10) C. W. Davies, H. W. Jones and C. B. Monk, *Trans. Faraday Soc.*, **48**, 921 (1952); M. S. Sherrill and A. A. Noyes, THIS JOURNAL, **48**, 1861 (1926).

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 $Pt(en)_3^{+4}$-Cl^- ion-pair at $I = 0.5$. At $[Cl^-] = 0.5$, $K_1 = 0.60$; $[Cl^-] = 0.4$, $K_1 = 0.66$; at $[Cl^-] = 0.30$, $K_1 = 0.68$; $[Cl^-] = 0.2$, $K_1 = 0.73$; and at $[Cl^-] = 0.1$, $K_1 = 0.75$. 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 $Pt(en)_3^{+4}$ with Cl^- and 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 Cl^- and 8 for Br^- association, reflect the identical charge of the two anions and the fact that Cl^- is but slightly smaller than Br^-.

The oxyanions studied provide an interesting series for comparison. Although the very large association of $SO_4^=$ can be understood in terms of its greater over-all charge, the difference between NO_3^- and ClO_4^- is not so obvious. Since the association of 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 π bonding in oxyanions from which approximate partial charges can be assigned to the O atoms in each of the anions studied.[11] These are $-{}^3/_4$ for $SO_4^=$, $-{}^2/_3$ for NO_3^- and $-{}^1/_2$ for 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 $SO_4^=$ than for Cl^- indicates the importance of the over-all charge of the ion.

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[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[1]

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 hexacoördination 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 hexacoördinated 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.[2] 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.[3] Due to the great stability of the phthalocyanine ring system, this unusual partly predetermined hexacoördination 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 inorganic 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.

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[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).