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# Complexes of Germanium(IV) with Anions of *o*-Diphenols and Their Stability Constants

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Complex formation between Ge(IV) and anions of substituted *o*-diphenols has been studied and stability constants are reported for 1:3 complexes. Correlations are established with the *o*-diphenol acidity constants and with the stability constants of 1:3 Si(IV) and 1:1 Cu(II) and Zn(II) complexes.

## Introduction

Solutions of germanium dioxide in water are those of an uncharged weak acid present as a mononuclear species, usually written $Ge(OH)_4$.[1] There is no evidence for cationic hydroxogermanium(IV) species in acid media; the addition of $HClO_4$, $HNO_3$, $H_2SO_4$, and HCl (up to 4.5 *M*) merely decreases the $GeO_2$ solubility and in a manner indicative of a salting-out effect.[2] The complex chemistry of Ge(IV) in aqueous solution is thus limited, and similar to that of As(III) and other elements which are present as hydrated oxides in acid media. Stable chelates are formed with polydentate oxygen-containing ligands and particularly with polyhydroxy compounds. With $H_2L$ *o*-diphenols, Ge(IV) appears to give largely $GeL_3^{2-}$ complexes;[3,4] however, $GeL_2 \cdot 2H_2O$ compounds have been isolated[5] and $HGeL_3^-$ has also been postulated.[6] The stability constants for Ge(IV) complexes with a series of *o*-diphenols have been determined to establish whether the correlation often noted for aquo metal ions between complex stability and ligand basicity[7] holds for Ge(IV). As a preliminary step, the nature of the Ge(IV) complexes formed with the 3,5-disulfonate *o*-diphenol derivative was investigated.

## Experimental Section

**Materials.**—Catechol (*o*-dihydroxybenzene) (British Drug Houses) was twice recrystallized from benzene; mp 105° (lit.[8] 105°). 4-Chlorocatechol (Aldrich Chemical Co.) was recrystallized several times from petroleum ether (bp 60–90°); mp 86° (lit.[9] 85–86°); potentiometric titrations with sodium hydroxide after addition of germanium dioxide indicated a 99% purity for the reagent. 4-Nitrocatechol was prepared by nitration of salicylaldehyde[10] and oxidation of the nitrosalicylaldehydes with hydrogen peroxide.[11] 4-Nitrocatechol was purified from the 3-nitro and dinitro isomers by washing with hot petroleum ether (bp 60–90°) and two crystallizations from benzene; mp 173–174° (lit.[12] 173–175°); potentiometric titrations with sodium hydroxide showed the reagent to be 99% pure. Sodium salts of catechol 3,5-disulfonate (Tiron) and 2,3-dihydroxynaphthalene 6-sulfonate (abbreviated DHNS) (Aldrich Chemical Co.) were recrystallized three times from boiling water and dried at 105° under nitrogen. Potentiometric titrations with sodium hydroxide after exchange of $Na^+$ for $H^+$ on Dowex IRA-120 or after addition of an excess of germanium dioxide gave assays of 94.5 ± 0.3% for Tiron and 97.1 ± 0.3% for DHNS. One sample of DHNS dried at 150° under 1–2 torr gave by the same titration methods 100.2 ± 0.3%, indicating 0.5 mole of water of crystallization in the product. The Tiron sample would similarly contain 1 mole of water. Ge(IV) stock solutions $4 \times 10^{-2}$ *M* were prepared from semiconductor grade $GeO_2$ (kindly supplied by the Germanium Research Center) and standardized by titration with sodium hydroxide after addition of mannitol. Other chemicals were reagent grade.

**Measurements.**—The ligand solutions were prepared in boiled distilled water saturated with nitrogen and brought to pH ~4 with hydrochloric acid. They were used within 3 days, during which their absorbance remained constant. Spectra were obtained on a Bausch & Lomb 505 recording spectrophotometer, and the optical absorbances were measured with a Zeiss PMQ-11 spectrophotometer using 0.2–10-mm quartz cells. Some runs were made using a flow cell hooked up by means of Tygon tubing to a peristaltic pump and a thermostated beaker. The composition of the solution which was circulated was varied by addition of a concentrated reagent solution. The pH measurements were made with a Radiometer Model 4 pH meter. The pH scale was calibrated for hydrogen ion concentration by using dilute hydrochloric acid in sodium chloride solutions of the required ionic strength. All experiments were made at 25.0 ± 0.1° under a nitrogen atmosphere.

**Calculations. (a) Ligand Acidity Constants.**—The acidity constants $K_1$ and $K_2$ of the *o*-diphenols $H_2L$ were evaluated from the effect of pH on the absorbance *A*. The $10^3$–$10^4$ ratios of $K_1$ to $K_2$ make it possible to determine each one separately. For example, with $K_2 = [H^+][L^{2-}]/[HL^-]$ and $C_L = [L^{2-}] + [HL^-]$, the following equation is derived

$$[H^+]\Delta A = K_2 C_L \Delta\epsilon_L - K_2 \Delta A$$

where

$$\Delta A = A - \epsilon_{HL} C_L = (\epsilon_L - \epsilon_{HL})[L^{2-}] = \Delta\epsilon_L [L^{2-}]$$

A plot of $[H^+]\Delta A$ against $\Delta A$ should be a straight line for $C_L$ constant with $-K_2$ as the slope. The wavelength was selected to give a maximum value for $\Delta A$. The values obtained for the stronger acid 4-nitrocatechol were checked by analysis of the neutralization curve.

**(b) Complex Stability Constants.**—Three spectrophotometric

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[1] (a) N. Ingri, *Acta Chem. Scand.*, **17**, 597 (1963); (b) the abbreviation $GeO_2$ is used here.

[2] (a) G. Brauer and H. Müller, *Z. Anorg. Allgem. Chem.*, **287**, 71 (1956); (b) R. L. Benoit and P. Clerc, *J. Phys. Chem.*, **65**, 676 (1961).

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methods were used to determine the stability constants. The conditional concentration constant for a complexing reaction between $GeO_2$ (abbreviated M) and $H_2L$ at a given pH is

$$\beta^*_n = \frac{[ML_n]}{[M][H_2L]^n}$$

$\beta^*_n$ is expressed as

$$\beta^*_n = \frac{\Delta A/\Delta\epsilon_n}{(C_M - \Delta A/\Delta\epsilon_n)(C_L - n\Delta A/\Delta\epsilon_n)^n}$$

where

$$\Delta A = A - \epsilon_{H_2L}C_L = (\epsilon_{ML_n} - n\epsilon_{H_2L})[ML_n] = \Delta\epsilon_n[ML_n]$$

$C_M$ and $C_L$ are the total concentrations of Ge and ligand, respectively. In the first method (1) used, $C_L$ is held constant and $C_M$ varied so that $[ML_n]$ is negligible with respect to $C_M$ and the previous equation may be rearranged as

$$(\Delta A/C_M)^{1/n} = (\beta^*_n C_L{}^n \Delta\epsilon_n)^{1/n} - n\beta^*_n{}^{1/n}\Delta\epsilon_n{}^{(1-n)/n}\Delta A$$

$\beta^*_n$ is calculated from the intercept and the slope of the straight line obtained by plotting $(\Delta A/C_M)^{1/n}$ against $\Delta A$. The second method (2) used to determine $\beta^0_3$ for the 1:3 complexes was that of Vareille.[13] When pH >2, the predominant complexing reaction is

$$GeO_2 + 3H_2L \rightleftarrows GeL_3{}^{2-} + 2H^+ + 2H_2O \qquad (1)$$

with

$$\beta^0_3 = \frac{(\Delta A/\Delta\epsilon_n)[H^+]^2}{(C_M - \Delta A/\Delta\epsilon_n)(C_L - 3\Delta A/\Delta\epsilon_n)^3}$$

$\Delta A$ reaches a maximum value $\Delta A_m$ for pH 5–6; this indicates that $GeL_3{}^{2-}$ is completely formed. Then, from the absorbance, $\Delta\epsilon_n = \Delta A_m/[GeL_3{}^{2-}]$ is obtained and introduced in the above equation to calculate $\beta^0_3$ for each point of the experimental curve giving $\Delta A$ against pH. Finally, with Tiron as a ligand, the corresponding solutions method (3) such as described by Fronaeus[14] was used; the values of $\beta^*_n$ were calculated according to Rossotti's procedures.[15]

## Results

Complexing with Tiron was studied first. The stoichiometry and equilibrium constants of the complexing reactions were established at 0.10 *M* [H⁺] by the corresponding solutions method (3), then $\beta^*_2$ was checked by method 1 at 0.50 *M* [H⁺] under conditions where 1:3 species are unimportant. The effect of ionic strength on $\beta^0_3$ was determined by method 2 at pH >2, where 1:2 complexes are not formed. Experimental conditions and results are summarized in Table I.[16]

The continuous variations method gives, at low acidity, sharp peaks indicative of 1:3 species.[4,16]

TABLE I

LOG $\beta_n$ VALUES FOR TIRON COMPLEXES AS A FUNCTION OF $H^+$ AND SODIUM CHLORIDE CONCENTRATIONS

| NaCl, *M* | pH range | $C_L$, m*M* | $C_M$, m*M* | λ, mμ | log $\beta^0_3$ | log $\beta^*_3 \cdot \lvert H^+\rvert^2$ | log $\beta^*_2$ | log $\beta^*_1$ |
|---|---|---|---|---|---|---|---|---|
| 1.00 | 0.10 *M* [H⁺] | 0–24.0 | 1.00–4.00 | 320 | | 3.6 | 3.90 | <1 |
| 0.50 | 0.50 *M* [H⁺] | 2.00 | 16.2–32.4 | 305 | | | 3.88 | |
| 0.110 | 3.3–4.0 | 0.200 | 20.2 | 305 | 2.30 | | | |
| 0.260 | 2.9–3.8 | 0.200 | 20.2 | 305 | 3.10 | | | |
| 0.50 | 2.3–4.0 | 0.500 | 24.5 | 306 | 3.50 | | | |
| 0.50 | 2.3–4.0 | 0.500 | 24.5 | 255 | 3.50 | | | |
| 1.00 | 3.0–6.0 | 0.500 | 0.326 | 305 | 3.70 | | | |

The spectrophotometric determinations of the *o*-diphenol acidity constants in 0.100 *M* KCl gave the following values[16] for $pK_1$ and $pK_2$, respectively: catechol, 9.39, 13.1; 4-chlorocatechol, 8.62, 12.55; 4-nitrocatechol, 6.77, 10.88; potentiometry led to 6.78, 10.95 for the latter compound.

The stability constants $\beta^0_3$ of the complexes with 4-chloro- and 4-nitrocatechols and DHNS were determined at low acidity for a 0.100 *M* KCl medium by method 2; method 1 was also used with the 4-nitro derivative. Data and results are summarized in Table II.[16] Detailed experimental data for the 4-nitrocatechol complex are presented in Table III and Figure 1.

TABLE II

LOG $\beta^0_3$ VALUES FOR 1:3 COMPLEXES OF 4-CHLORO- AND 4-NITROCATECHOLS AND DHNS

| Ligand | pH range | $C_L$, m*M* | $C_M$, m*M* | λ, mμ | log $\beta^0_3$ |
|---|---|---|---|---|---|
| 4-Chlorocatechol | 3.4–5.7 | 1.43 | 0.408 | 300 | 0.65 |
| 4-Nitrocatechol | 2.4–4.4 | 0.754 | 0.204 | 400 | 3.90 |
| | 2.00 | 0.710 | 1–16 | 400 | 3.85 |
| DHNS | 3.6–5.4 | 0.295 | 0.0408 | 256 | 2.0 |

TABLE III

DETERMINATION OF LOG $\beta^0_3$ VALUES FOR THE 1:3 COMPLEX OF 4-NITROCATECHOL BY METHOD 2

| pH[a] | $\Delta A$[b] | log $\beta^0_3$[c] |
|---|---|---|
| 2.00 | 0.017 | |
| 2.40 | 0.059 | 3.91 |
| 2.48 | 0.076 | 3.93 |
| 2.59 | 0.082 | 3.78 |
| 2.66 | 0.119 | 3.95 |
| 2.97 | 0.198 | 3.96 |
| 2.99 | 0.203 | 3.94 |
| 3.17 | 0.244 | 3.92 |
| 3.49 | 0.306 | 3.86 |
| 3.68 | 0.342 | 3.89 |
| 3.98 | 0.382 | 3.89 |
| 4.37 | 0.415 | 3.88 |
| 5.19 | 0.438 | |
| 5.61 | 0.445 | |

[a] $C_L$ = 0.754 m*M* and $C_M$ = 0.204 m*M*. [b] λ 400 mμ, 1.00-mm cell. [c] Calculations made on the basis of $\Delta A_m$ = 0.435.

## Discussion

According to previous results,[3-6] the predominant complexing reactions to consider between $GeO_2$ and *o*-diphenols are

$$GeO_2 + 3H_2L \rightleftarrows GeL_3{}^{2-} + 2H^+ + 2H_2O \qquad (1)$$

$$GeO_2 + 2H_2L \rightleftarrows GeL_2 + 2H_2O \qquad (2)$$

The detailed study of the $GeO_2$–Tiron system confirms these views. The 1:2 species can only be identified at high acidity where the 1:3 complex is less formed.

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(16) Material supplementary to this article has been deposited as Document No. 9443 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $3.75 for photoprints, or $2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

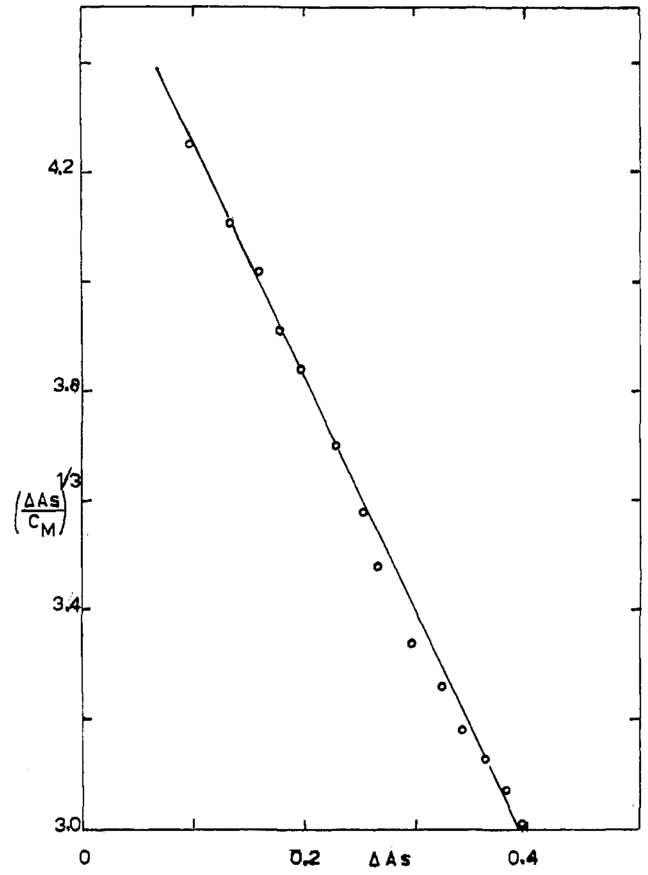

Figure 1.—Data used in the evaluation of log $\beta^0_3$ for the 1:3 complex of 4-nitrocatechol: $C_L$ = 0.710 m*M*; $C_M$ = 1–16 m*M*; pH 2.00; λ 400 mμ, 2.00-mm cell.

The corresponding solutions method (3) gives $\beta^*_2 = 10^{3.90}$ at 0.1 *M* [$H^+$], and at 0.5 *M* [$H^+$] the same value, $\beta^*_2 = 10^{3.88}$, is found by method 2. This indicates that the effect of acidity on the 1:2 complex formation is adequately represented by reaction 2. The complex is probably better written $GeL_2(OH_2)_2$ since 1:2 base adducts of $GeL_2$-type chelates have recently been prepared from nonaqueous solutions.[17] That two different methods give the same $\beta^0_3$ values, $10^{3.70 \pm 0.05}$ between pH 3 and 6 and $10^{3.6}$ at 0.1 *M* [$H^+$], supports reaction 1 and further indicates that $HGeL_3^-$ is a strong acid, contrary to the views of Nazarenko and coworkers.[6] These authors, on finding that the $H^+$ concentration produced by adding $GeO_2$ to catechol and pyrogallol solutions is lower than that calculated from reaction 1, assumed incomplete ionization for $HGeL_3^-$. The high concentrations used are such that the formation of $GeL_2$ also accounts for these results, and by using the data of the authors, fairly constant values could be obtained for log $\beta_2$.

The absence of 1:1 complexes, shown with Tiron ($\beta^*_1 < 10$), confirms the results obtained with other classes of ligands[18] and is attributed to the strong hydration of $GeO_2$ in solution. The formation of polynuclear species appears unimportant as $\beta^0_3$ values are not affected when $C_M$ is varied between 0.3 and 4 m*M* (Tiron, Table I) and 0.2 and 16 m*M* (4-nitrocatechol, Table II). This result is also in line with previous studies of other oxygen-containing ligands.[18]

The effect of ionic strength (NaCl) on $\beta^0_3$ values as shown in Table I is large; this is apparently due to the −8 charge on the complex resulting from the sulfonate groups. Log $\beta^0_3$ was plotted against $\mu^{1/2}$ and compared with values obtained for KCl media.[19] Both curves coincide up to $\mu$ = 0.16 *M;* above this value there is a specific cation effect. Such an effect has already been noted for the Al(III)–Tiron system.[20] The ionic strength influence is much smaller for the catechol and pyrogallol complexes,[8] which bear a −2 charge.

The study of the $GeO_2$–Tiron system further indicates that the effect of ligand substituents on the stability of the Ge(IV) complexes with *o*-diphenols can be investigated with the 1:3 complexes which are the only ones formed at relatively low acidity. The absence of 1:2 complexes in the pH ranges used (Table II), indicated by the constant $\beta^0_3$ values found, is further justified by the very low Δ*A* values (Table III) obtained at the lowest pH. The 1:2 and 1:3 complexes have similar spectra and related ε values, so that an appreciable concentration of $GeL_2$, which is not acidity dependent, would have given a notable Δ*A* at low pH where $GeL_3^{2-}$ is not formed.

The available values of p$K_1$, p$K_2$, and log $\beta^0_3$ ($\mu$ = 0.10 *M*) for the various ligands and the corresponding 1:3 Ge(IV) complexes are collected in Table IV.

TABLE IV

SUMMARY OF p*K* AND LOG $\beta^0_3$ VALUES FOR IONIZATION AND COMPLEX FORMATION, RESPECTIVELY

| Ligand | p$K_1$ | p$K_2$ | Log $\beta^0_3$ | Log $\beta_3 K_{Ge}^{-1}$ |
|---|---|---|---|---|
| Catechol | 9.39 | 13.1 | −1.45[a] | 66.0 |
| 4-Chloro- | 8.62 | 12.55 | 0.65 | 64.2 |
| 4-Nitro- | 6.78 | 10.90 | 3.90 | 57.0 |
| Tiron | 7.66[b] | 12.6[b] | 2.30 | 63.1 |
| DHNS | 8.19[b] | 12.16[b] | 2.0 | 63.0 |
| Pyrogallol | | | −0.80[a] | |

[a] Reference 8. [b] Reference 21.

The values obtained for p$K_1$ are generally in good agreement with those previously reported. The p$K_2$ values are close to that known for the 4-nitro derivative but 1.00 higher for the 4-chloro one;[9] literature values for catechol[9,21] vary between 11.6 and 13. It is interesting to note that there is a linear relationship between the p$K_1$ and p$K_2$ values of the ligands, Tiron excepted. Such a relation, if extended to other substituents, could be explained in terms of Hammett σ constants.[22]

A fair linear correlation with a −1.1 slope is observed between the stability constants log $\beta^0_3$ of the complexes and the sum of the ligands acidity constants p$K_1$ + p$K_2$. The negative value of the slope is unusual for

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this kind of correlation and comes from the different definitions of $\beta^0_3$ for these germanium complexes and the usual aquo metal ion complexes. Defining as usual $\beta_3 = [GeL_3^{2-}]/[Ge^{4+}][L^{2-}]^3$, $\beta_3$ can be related to $\beta^0_3$ by means of $\log \beta_3 K_{Ge}^{-1} = \log \beta^0_3 + 3(pK_1 + pK_2)$, where $K_{Ge} = [GeO_2][H^+]^4/[Ge^{4+}]$ is a hypothetical hydrolysis constant. The $\log \beta_3 K_{Ge}^{-1}$ values given in the last column of Table IV are plotted against $pK_1 + pK_2$ in Figure 2; a +1.9 slope is now obtained. An interesting point is that the values of the stability constants corresponding to two other ligands whose conjugated acids are related to diphenols,[18] maltol (3-hydroxy-2-methyl-4-pyrone) and tropolone, fall on the line.

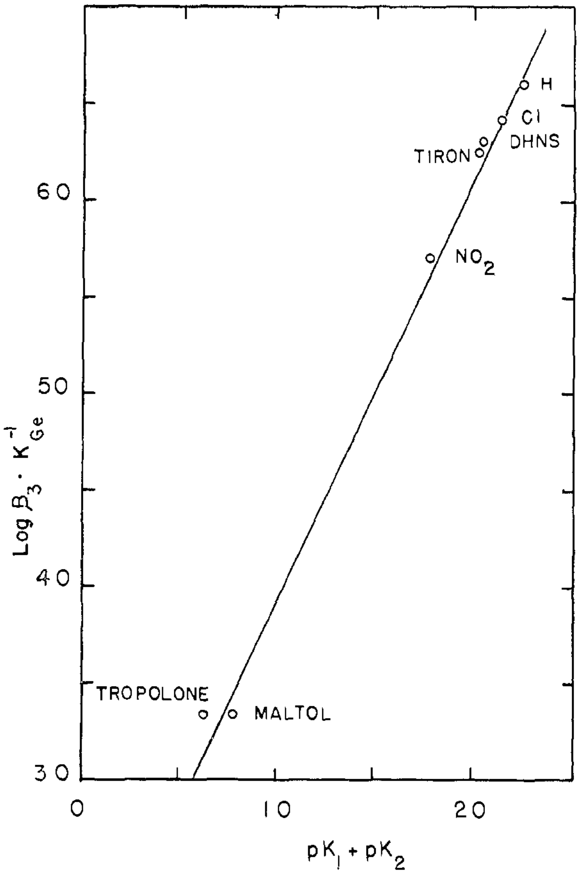

Figure 2.—The $\log \beta_3 K_{Ge}^{-1}$ *vs.* $pK_1 + pK_2$ values for Ge(IV) complexes with catechol derivatives, maltol, and tropolone: H, catechol; Cl, 4-chloro; $NO_2$, 4-nitro.

The limitations of the relations between complex stability and ligand basicity have been pointed out,[23] and wider correlations have been obtained by comparing stabilities of complexes for different pairs of metals.[23,24] Some complexes of Si(IV)[25] and divalent metals[9] with *o*-diphenols have already been studied so that such correlations can be tested with the present results. Values of $\beta^0_3$ for Si(IV) complexes (0.8 *M* KCl) are plotted in Figure 3 against those of $\beta^0_3$ for Ge(IV) complexes (0.1 *M* KCl except for Tiron, 0.8 *M* KCl); a straight line of slope 1.0 is obtained. Interpretation of this result in terms of a comparison of $\sigma$ and $\pi$ bonding contributions in the bonding of Ge and Si to the ligands appears unwarranted.[7] The stabilities of the Si(IV) and Ge(IV) complexes cannot be compared because of the unknown (although constant) degree of polymerization of silica in the experimental work of Bartels.[25]

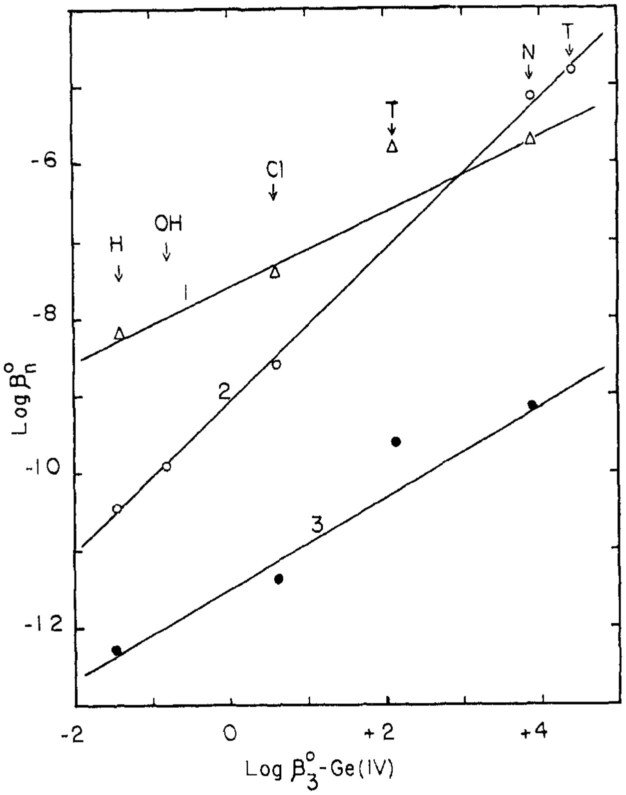

Figure 3.—The values of $\log \beta^0_n$ for 1:3 Si(IV) and 1:1 Cu(II) and Zn(II) complexes *vs.* $\log \beta^0_3$ for 1:3 Ge(IV) complexes with catechol derivatives: H, catechol; OH, pyrogallol; Cl, 4-chloro; T, Tiron; N, 4-nitro. (1) $\beta^0_1$, Cu(II); (2) $\beta^0_3$, Si(IV); (3) $\beta^0_1$, Zn(II).

Comparisons between stabilities of the complexes of Ge(IV) and those of Zn(II) and Cu(II) as determined by Murakami and co-workers[9] were made on the basis of new equilibrium constants $\beta^0_1$ such as $\beta^0_1 = [ZnL][H^+]^2/[Zn][H_2L]$. Values of $\beta^0_1$ were calculated as $\log \beta^0_1 = \log \beta_1 - (pK_1 + pK_2)$ from the authors' values of p*K* and $\beta_1 = [ZnL]/[Zn][L]$. This transformation offers the added advantage of eliminating possible errors in the difficult potentiometric determinations of $pK_2$, errors which would be included in the calculated $\beta_1$ values.[9] The results plotted in Figure 3 show a good correlation between $\log \beta^0_1$ for Zn(II) and Cu(II) and $\log \beta^0_3$ for germanium(IV), except for Tiron. Values of $\beta^0_2$ calculated for $ZnL_2$ complexes[9] indicate the same trend. By using the data available for Cu(II), Zn(II), and catechol and its 4-carboxy, chloro, sulfonate, and nitro derivatives,[9,26] fair straight lines were obtained when plotting $\log \beta^0_1$ against $pK_1$. This shows that the usual linear relationship holds between $\log \beta_1$

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and $pK_1 + pK_2$ (or $pK_1$, $pK_2$) if it is assumed that the linear relation between $pK_1$ and $pK_2$ can be extended to 4-carboxy and 4-sulfonate substituents. The failure of previous workers[9] to observe this relation between $\log \beta_1$ and $pK_1 + pK_2$ is apparently due to erroneous experimental values of $pK_2$ for catechol and its 4-chloro and carboxy derivatives. The effect of ligand substituents on the stability of *o*-diphenol complexes with Ge(IV), Si(IV), and divalent metals appears therefore to be in line with the general relations between complex stability and ligand basicity.

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# Polar Six-Coordinate Tin(IV) Complexes of Type $SnX_2L_2$: Synthesis, Structure, and Bonding

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The structures of several six-coordinate tin complexes of the type $SnX_2L_2$ have been studied, where X is Cl, Br, or I, and L is acetylacetonate or dibenzoylmethanate. Dipole moment measurements in benzene solution at 25 and 60° as well as nmr chemical shift data indicate that the complexes are of the *cis* configuration. Infrared and ultraviolet spectra suggest, respectively, that tin–halogen bonds are stronger than those of simple six-coordinate adducts, and that tin–oxygen bonds are primarily ionic in character. An improved method of synthesis has been reported for bromo and iodo derivatives.

The ability of silicon, germanium, tin, and lead to increase their coordination numbers beyond four has been attributed to the availability of empty d orbitals.[1] However, such orbitals belonging to an isolated atom are too diffuse for effective overlap with ligand orbitals. In fact, calculations[2-4] have shown that the d orbitals in question contract enough to allow the formation of bonds only in the presence of highly electronegative ligands.

The majority of investigations to date have concerned bonding in silicon compounds. Calculations[5] have demonstrated that about silicon the order of effectiveness of ligands in contracting 3d orbitals is $F > Cl > C \gg H$. A large body of experimental evidence indicates that for silicon compounds[6] there is effective overlap between ligand p orbitals and metal d orbitals to form $\pi$ bonds. Evidence for such $(p \rightarrow d)$ $\pi$ bonding is based largely on the analysis of bond characteristics such as bond lengths, bond energies, infrared spectra, and electric dipole moments. It has been suggested[7,8] that trends in donor and acceptor strengths of compounds of silicon and its heavier cogeners are strongly influenced by such $(p \rightarrow d)$ $\pi$ bonding effects, which decrease in magnitude as the central atom increases in size and as the d orbitals available for bonding become more diffuse. In particular, it is claimed that $(p \rightarrow d)$ $\pi$ bonding is very important in most silicon–oxygen bonds, of lesser importance for germanium–oxygen bonds, and small or nonexistent for tin–oxygen bonds. That does not mean that the orbitals of tin cannot be used for $\pi$ bonding with atoms other than oxygen. In fact, halogen atoms probably quite effectively contract the 5d orbitals of tin, since the acceptor properties of tin halides are well known.[1]

On the other hand, the nature of the bonding in true six-coordinate tin complexes has been investigated to only a very limited extent.[9] This is especially the case for compounds such as dichlorobis(2,4-pentanedionato)tin(IV).

Beyond doubt, $SnCl_2(acac)_2$ has been demonstrated to be monomeric in boiling benzene,[10] and it has been shown that nitrobenzene solutions are very poor conductors[11] of electricity. The disclosure that the molecule exhibits a large (8.8 D.) dipole moment[12] in benzene solution suggests that a *cis*-type configuration is likely. Recently, nmr and infrared data have been reported which are consistent with the assignment of a *cis* configuration.[13,14] Similar nmr data have been interpreted in terms of an unlikely equilibrium be-

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