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COORDINATION COMPOUNDS OF GERMANIUM

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CONTENTS

A. INTRODUCTION

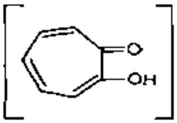
Analysis of the recent literature on germanium has made it apparent that in the past several years there has been an increased interest in the study of the various coordination compounds which this atom forms. Previous review articles have appeared in which various complexes of the Group IV elements are described, but in most instances germanium is either not treated in depth or is treated in relationship to a specific aspect. The present review summarizes in greater detail the recent work reported on the coordination compounds of germanium, covering primarily the work published since 1962. However, for the sake of continuity reference is sometimes made to previously reported studies.

B. HEXACOORDINATE SYSTEMS

To explore high-coordination, it is apparent from the existing literature that the more favorable ligands are (a) small atoms such as fluorine or hydrogen,

b) other metal atoms as in polyhedral boranes; and (c) polydentate ligands such as EDTA, ethylenediamine, nitrilotriacetate etc.[44]. The polydentate ligand has much to recommend it as a probe of high-coordination chemistry although one must be aware of steric factors that preclude high coordination numbers in certain complexes.

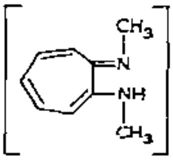
One bidentate ligand that is fairly compact by virtue of its coplanar ring structure is one derived from tropolone (I)



I

2-hydroxy-2,4,6-cycloheptatriene-1-one (T)

Considerable stability should he attrihuted to chelate structures based on this ligand because of the delocalization of π electrons. Related to the tropolone ligand is a structure (II) derived from *N,N'*-dimethylaminotroponimine (A).



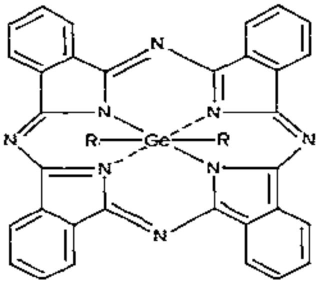
II

N.N'-dimethylaminotroponimine (A)

Muetterties and Wright[44,45] treated the tetrahalides of germanium with *N,N'*-dimethylaminotroponimine, or preferably its lithium salt, in chloroform to give octahedral A_3Ge^+ chelates. These cationic chelates were found to be thermodynamically unstable toward hydrolysis and could not be prepared in aqueous media. On the other hand tropolone and germanium tetrachloride gave T_3Ge^+ as the sole chelated product in aqueous media, while in non-aqueous media a material of the composition T_2GeCl_2 was obtained which could then be reacted with water to give T_3Ge^+.

These workers also reported the reaction T_3Ge^+, Cl^- with silver tropolonate in aqueous acetonitrile to give a pale orange solid of the composition $GeT_4 \cdot 2H_2O$. The proton n.m.r. spectrum of $GeT_4 \cdot 2H_2O$ showed two bands of aromatic CH resonance, one multiplet characteristic of the chelate and one characteristic of the tropolone anion. Thus, this orange solid, they contend, must be the tropolone salt of the chelate cation $GeT_3{}^+$. *In vacuo*, $GeT_4 \cdot 2H_2O$ dehydrated to black microcrystals of GeT_4. Although all available spectroscopic data (infrared and n.m.r.) suggested that this black chelate is the primary salt, *i.e.*, $GeT_3{}^+T^-$, the integration of the chelate to anion resonances consistently showed a ratio of chelate to anion greater than 3:1. These n.m.r. results raised the possibility of a solution equilibrium between the salts and a seven – or eight – coordinate structure. Attempts to appraise this hypothesis by varying the dielectric constant of the medium failed because of the reactivity of the anhydrous chelate towards most solvents.

Kenney and co-workers[29,32,18,56,60] report and describe specific germanium phthalocyanines. These compounds are important because few metal phthalocyanines are known in which the central element has as large an electronegativity as germanium. Also, they provide an opportunity for the study of hexacoordinate germanium when it is bonded to six atoms of which four are nitrogen atoms; the four nitrogen atoms and the germanium atom can be assumed to be in a planar arrangement. Due to the great stability of the phthalocyanine ring system, this unusual, partly predetermined, hexacoordination of germanium is preserved under a wide variety of conditions (III)



III

The germanium phthalocyanines are also notable in that they exhibit a functionality associated with the two non-ring atoms (R) bonded to the germanium—a kind of functionality which is seldom fully utilized in phthalocyanine chemistry[29]. The use of this inorganic functionality in synthesizing a series of substituted germanium phthalocyanines, and exploitation of the stable phthalocyanine ring, controlling the number and positions of atoms around the germanium, are described by Kenney and co-workers[18,29,32,56,60].

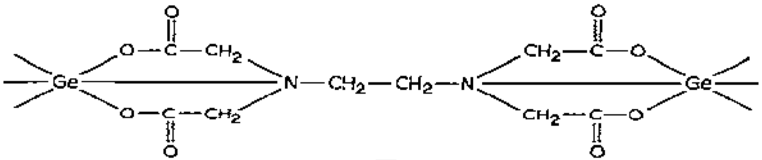
Simpler systems of germanium having hexacoordination are described by Aggarwal and co-workers[1,3]. Using 4d orbitals, Ge in GeF_4 increases its covalency from 4 to 6 with GeF_4 acting as a Lewis acid. In this manner GeF_4 forms 1:2 complexes with ethers, acetone, and methyl alcohol[1]. Similarly, it also forms 1:1 adducts with ethylenediamine and 1:2 complexes with acetonitrile, ammonia, hydrazine, pyrrolidine, and piperidine. The nitrogen-containing complexes are white, non-volatile, thermally stable solids, insoluble in hydrocarbons. The related oxygen-containing complexes are stable at 25 °C, except for acetone and ethylene oxide.

Germanium tetrafluoride also forms 1:1 and 1:2 complexes with hydrogen sulfide, methyl mercaptan, dimethyl sulfide, tetrahydrothiophene, and tetrahydrothiopyran[2]. The complexes $GeF_4 \cdot H_2S$, $GeF_4 \cdot (MeSH)_2$, and $GeF_4 \cdot MeSH$ are unstable at 25°. The remaining compounds melt below 100°, except $GeF_4 \cdot H_2S$ which melts above 300°.

Langer[40] describes a new convenient way for preparing pure crystalline chelates of germanium with ethylenediamine tetraacetic acid (EDTA). The most interesting feature of the preparation of EDTA chelates with the tetravalent metal is its simplicity. A pure product is obtained by interacting metal tetrachlorides with disodium EDTA. This is possible because of the following properties of Group IV metal EDTA chelates:

(1) The compounds of the type $M(EDTA) \cdot xH_2O$ are stable at pH 1.5 and are not appreciably dissociated into M^{+4} cations and EDTA anions.
(2) The chelates are weak acids.
(3) The chelates are only slightly soluble.
(4) The products are well crystallized with no inclusion of sodium or chloride ions.

From a comparison of analytical data, infrared spectra, and dehydration experiments for the crystalline chelate and its sodium salts, structures are proposed for these compounds. In the case of germanium, Langer, basing his argument on steric hindrance, does not favor a mononuclear structure in which two nitrogen atoms and four acetate groups of an EDTA molecule are co-ordinated to a single germanium atom. For the same reason the co-ordination number eight is not considered. He ascertains that the sharp carbonyl band at 1730 cm^{-1} points strongly to a binuclear arrangement (IV)



IV

Based on Langer's work, Clark, Davies, and Jones[8] have also assigned a similar binuclear arrangement to the straight-chain α-hydroxy acid complexes of germanium. Analysis shows these solids to be of the general formula $R_2C_4H_2O_6Ge \cdot 2H_2O$, where R is an alkyl group. On heating to 120–130° these solids lose 2 molecules of water and form the anhydrous compound of the general formula $R_2C_4H_2O_6Ge$.

Prior to his work with α-hydroxy acids, Clark reported the reaction between some organic thio-acid and germanic acid in aqueous solution[9]. These acids form 1:2 complexes and appear to be decomposed gradually as titration with alkali proceeds beyond pH 6.0.

In 1964, Cox, Lewis and Nyholm reported the reactions of several β-diketones with the Group IV tetrachlorides[14]. An interesting rearrangement of the type

$$MCl_4 + Fe(diketone)_3 \rightarrow [M(diketone)_3]^+ + FeCl_4^-$$

occurs when certain of the Group IV tetrahalides react with a tris-β-diketone iron(III) complex in solution. For metals, where the tris-diketone cation is not produced, a non-electrolyte of the type $[M(diketone)_2Cl_2]^0$ or $[M(diketone)_3Cl]^0$ is produced in this reaction. For germanium, rearrangement of the acetylacetone ligands (acac) gave the complex $[Ge(acac)_3]^+FeCl_4^-$: This type of cation is well

TABLE I

HEXA COORDINATED SYSTEMS

Compound	*Reference*	*Compound*	*Reference*
$Ge[(CH_2)O]_2F_4$	1	$PcGe(NCO)_2$	60
$Ge[(CH_2)_4O]_2F_4$	1	$PcGe(NCS)_2$	60
$Ge[(CH_2)_5O]_2F_4$	1	$PcGe(NCSe)_2$	60
$Ge[CH_3)_2O]_2F_4$	1	$GeO_2 \cdot$ Alizarine Red S	21
$Ge[(CH_3)_2CO]_2F_4$	1	$GeI_4 \cdot 4C_6H_5N_2H_3$	24
$Ge(CH_3OH)_2F_4$	1	$GeBr_4 \cdot 4C_6H_5N_2H_3$	24
$Ge[O(CH_2)_4O]F_4$	1	$GeI \cdot 4NO_2C_6H_4N_2H_3$	24
$Ge[H_2N(CH_2)_2NH_2]F_4$	2	$GeBr_4 \cdot 4NO_2C_6H_4N_2H_3$	24
$Ge(CH_3CN)_2F_4$	2	$LiAlGeO_4$	34
$Ge(NH_3)_2F_4$	2	$LiAlGeO_6$	34
$Ge(N_2H_4)F_4$	2	$NaAlGeO_4$	34
$Ge(pyrrolidine)_2F_4$	2	$LiAlGe_3O_9$	34
$Ge(piperidine)_2F_4$	2	$Li_2NaAlGe_3O_9$	34
$Ge(H_2S)_2F_4$	2	$LiKAlGe_3O_9$	34
$Ge[(CH_3)_2SH]_2F_4$	2	$KAlGeO_4$	34
$Ge[(CH_3)_2S]_2F_4$	2	$RbAlGeO_4$	34
$[GeR'_2(OH)_2]^{2-}$	6	$CsAlGeO_4$	34
$R_2C_4H_4O_6Ge \cdot 2H_2O$	8	$[GeF_n(OH)_{6-n}]^{2-}$; $n = 0$ to 6	35, 36
$R_2C_4H_2O_6Ge$	8	$Na_4(GeF_{10}O)$	35, 36
$Ge(OH)_4 \cdot R_2''$	9	$K_4(Ge_2F_{10}O)$	35, 36
$CF_3GeF_3 \cdot 2F^-$	10	$GeY \cdot 2H_2O$	40
$Ge(OH)_2Q_2$	11, 15, 64	GeY	40
$[Ge(acac)_3]Cl$	14	$GeCl_4 \cdot 2(CH_3)_2SO$	41
$[Ge(acac)_2Cl]^0$	14, 15	$GeX_4 \cdot 2L$	42
$[Ge(acac)]^+FeCl_4^-$	14, 15, 43	$[T_3Ge]^+Cl^-$	44, 46
$PcGeF_2$	18	$[T_3Ge]^+PF_6^-$	44
$PcGeBr_2$	18	$[A_3Ge]^+I^-$	44
$PcGeI_2$	18	GeT_4	44
$HpGeF_2$	18	$GeT_4 \cdot 2H_2O$	44
$HpGeBr_2$	18	$[T_3Ge]^+Br^-$	46
$HpGeCl_2$	18	$[T_3Ge]^+I^-$	46
$HpGe(OH)_2$	18	$[A_3Ge]^+Br^-$	49
$(HpGeO)_x$	18	$[GeCl_4(HC_4H_4O_6)_2]^{2-}$	53
$HpGe(OC_4H_9)_2$	18	$[GeCl_2(C_4H_4O_6)_2]^{2-}$	53
$HpGe(OC_2H_5)_2$	18	$GeRhLiO_4$	16
$(PcGeO)_x$	18	$LiCrGeO_4$	16, 65
$PcGeCl_2$	29, 32	$Cs_2[GeCl_6]$	67
$PcGe(OH)_2$	29, 32	$Rb_2[GeCl_6]$	67
$PcGe(OPh)_2$	29, 32	$(N(CH_3)_4)_2[GeCl_6]$	67
$PcGe(OC_6H_5Ph\text{-}p)_2$	29, 32	bis(*o*-phenylenedioxy)germane-bis(triethylamine)	68
$PcGe(OSiPh_3)_2$	29, 32		
$PcGe(OCOCH_3)$	56	bis(*o*-phenylenedioxy)germane-bis(dimethylformamide)	68
$PcGe(OC_4H_9)_2$	56		
$PcGe(OC_8H_{17})_2$	56	bis(*o*-phenylenedioxy)germane-dipyridine	68
$PcGe(OCH_2CH_2SH)_2$	56		

R′: various 2,5-dihydroxy-*p*-benzoquinone derivatives
R: alkyl group
R″: aliphatic thioacids
Q: 8-hydroxyquinoline
Acac: acetylacetone
Pc: phthalocyanine
Hp: hemiporphyrazine
Ph: phenyl
Y: EDTA anion
L: pyridine and isoquinoline
T: tropolone
A: *N,N′*-dimethylaminotroponimine

known in the case of silicon. The reaction between $[Ge(acac)_2Cl_2]^0$ and iron(III) chloride occurs readily, and other derivatives of the $[Ge(acac)_3]^+$ ion can be obtained in a similar manner.

Complex compounds of tetravalent germanium with phenyl—and *p*-nitrophenylhydrazine were also prepared[24]. The thermal stability of these salts increases from iodide to bromide; it is greater for the nitrophenylhydrazine derivatives as established from the corresponding differential thermal diagrams. Infrared measurements indicate that the compounds are hexacoordinated with an octahedral *trans*-configuration.

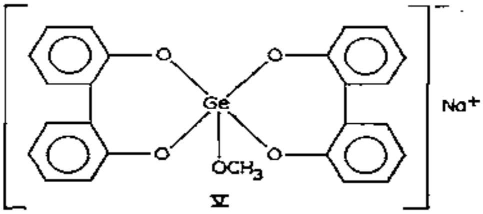
The stability and formation of complexes between germanic acid and 8-hydroxyquinoline (Q) were investigated by Clerc[11]. The compound $[Ge(OH)_2Q_2]$ precipitates slowly and partially from solutions. Corroborating determinations indicate that this behavior is attributable to a *cis-trans* isomerization of the complex. Clerc suggests that the initial complex is of *cis*-octahedral configuration which, after internal rearrangement to the more stable *trans*-form, slowly precipitates from solution.

Other hexacoordinated germanium compounds include, as ligands, various substituted 2,5-dihydroxy-*p*-benzoquinones[6], substituted *o*-diphenols[30,54], and dimethylsulfoxide[41]. Many hexachlorofluorohydroxo-, oxyfluoro-, and aluminogermanates are also reported[27,28,34,36,67]. All these and other complexes are tabulated above (Table 1).

C. COORDINATION SYSTEMS LESS THAN SIX

Evidence for other possible coordination systems of tetravalent germanium is somewhat limited. As noted above, germanium tetrafluoride increases its covalency when GeF_4 acts as a Lewis acid. It forms 1:1 complexes with MeCN, PH_3, H_2S, MeSH and Me_2S (see Table 2). The stability of these compounds are similar to their respective 1:2 analogous.

Mueller and Heinrich[43] report a complex which they refer to as a pentavalent central Ge atom. They found that the titration of (2,2′-biphenylenedioxy) germane (B) with sodium methoxide gave rise to Na[B(OMe)] (V)



V

The possibility of other coordinated germanium complexes is suggested by

TABLE 2

Ge COORDINATION SYSTEMS LESS THAN SIX

Coordination of 5 Ge^{IV}	*Reference*
$Ge(MeCN)F_4$	2
$Ge(PH_3)F_4$	2
$Ge(PMe_3)F_4$	2
$Ge(H_2S)F_4$	2
$Ge(MeSH)F_4$	2
$Ge(Me_2S)F_4$	2
$Na[Ge(2,2'\text{-biphenylenedioxy})_2(OMe)]$	43
Coordination of 4 Ge^{II}	
$Ge(C_4H_8O_2)Cl_2$	37
$I_2Ge[Fe(CO)_2(\pi\text{–}C_5H_5)]_2$	20
$Cl_2Ge[Fe(CO)_2(\pi\text{–}C_5H_5)]_2$	20
$H_2Ge[Fe(CO)_2(\pi\text{–}C_5H_5)]_2$	20
$Me_2Ge[Fe(CO)_2(\pi\text{–}C_5H_5O)_2$	20
$H_4[Ge(Mo_3O_{10})_4] \cdot nH_2O$	31
Coordination of 3 Ge^{II}	
$[GeF_3]^-$	47
$Ge(R_3P)I_2$	33

Gielen and Sprecher in their review article dealing with the coordination of Group IV elements[22].

Coordination numbers of four and three are attributed to some germanium complexes, but here germanium is in the divalent state. For instance, germanium dichloride complexes with 1,4-dioxane to yield $Ge(C_4H_8O_2)Cl_2$ This complex[37] is stable in air and is hydrolyzed to $Ge(OH)_2$ by H_2O. It decomposes at 140–210 °C.

The chemistry of the difluorides of germanium and tin is reported by Muetterties[47]. The formation of complexes between these fluoride salts of Ge^{II} and F^- are described. In such cases the coordination number of germanium is three. This appears also to be the case with the complexes reported hy King[33]. He treated germanium(II) iodide with various alkyl and aryl phosphine derivatives and formed adducts of the general formula $Ge(R_3P)I_2$. These compounds are air sensitive and soluble in certain organic solvents.

D. STEREOCHEMISTRY

Based on infrared and nuclear magnetic resonance spectroscopy, it is possible to assign a *cis*-configuration to the bis-chelated acetylacetone complex of germanium[57], $[Ge(acac)_2Cl_2]$. Similarly, infrared measurements indicate that the complex compounds of tetravalent germanium with phenyl- and *p*-nitrophenylhydrazine are 6-coordinated with an octahedral *trans*-configuration[24].

As noted above, Langer[40] proposes a binuclear structure for the EDTA complexes, in which steric hindrance does not favor a mono-nuclear structure. The single sharp carbonyl band observed in the infrared spectra of these complexes points strongly to this binuclear arrangement (see (IV)). A combination of the covalent character of the metal-carboxylate bond, the inductive effect of coordinated nitrogen, and the absence of electron withdrawing groups near the carbonyl oxygen is thought to be responsible for the high carbonyl frequency at 1730 cm^{-1}, which is 41 cm^{-1} higher than that of the EDTA molecule.

As was mentioned earlier in this review, Clark and his co-workers[8] suggested a similar binuclear arrangement with germanium having a coordination number of six. This was based on the similarity between their complexes and the EDTA complexes of Langer[40]. The added fact tbat the presence of ionic carboxylate groups in the dihydrate was not indicated by infrared spectra also led to the above conclusion.

Clerc[11] postulated that the reaction of 8-hydroxyquinoline in an aqueous solution of germanic acid leads initially to the more probable *cis*-dihydroxobis-(8-hydroxyquinoline)germanium(IV) complex. This complex then precipitates in the more thermodynamically stable *trans*-form. From the point of view of probability and geometry, the *cis*-form is favored since a total of eight isomers are possible. From the point of view of thermodynamics, however, the *trans*-configuration is more stable and the internal *cis*/*trans*-conversion of the OH groups is assigned a ΔH value of -6 Kcal/mole. The dispositions, *cis* and *trans*, are relative to the OH groups.

In Kenney's investigation of the germanium phthalocyanine complexes, a study of figure (III) reveals the fact that there is but one possible configuration[18,29,32,56,60]. The four nitrogens are assumed to be in a planar arrangement and the two functional groups are, therefore, *trans* to each other.

Though infrared and nuclear magnetic resonance spectra are the principal techniques used to probe into chemical structure, other methods have also been employed. For instance, Karnatak and Sakellarids[30] studied X-ray absorption of the phenol and diphenol complexes of germanium. The absorptions were indicative of the type of ligands, the stereochemistry of the complex, and the nature of the bonds between the ligands and the central metal ion.

E. SPECTROSCOPY

Since the stereochemistry of many of the complexes of germanium have been determined from spectroscopic information, it is important to consider the assignment and interpretation of the specific group frequencies and relate them to the appropriate structural features.

Smith and Wilkins[59] have proposed the probable structure of selected germanium complexes on the basis of their n.m.r. spectrum. $Ge(acac)_2Cl_2$ is assigned a *cis*-configuration. Peaks in the methyl region appeared at 7.77, 7.89 and 7.96 τ. The peak at 7.77 was unsymmetrical and appeared to be superimposed over a weaker peak at 7.78. Thus one could reasonably argue in favor of four carbonyl group adjacent to the methyl group. A *trans*-configuration for this complex would yield a symmetrical molecule from which four methyl peaks would not be anticipated. The values of these peaks are close to those of the methyl signals in the enol and keto-forms of the free ligands. Stronger evidence for this *cis*-configuration in *bis*-chelated Ge^{IV} comes from the spectrum of $Ge(bzac)_2Cl_2$. The methyl region appears to have peaks at 7.57, 7.59, 7.61, and 7.76. This is consistent with a *cis* molecule, which can have three stereoisomeric forms, two forms each of which yield one signal, and the third which yields two signals, a total of four. A *trans*-configuration can have only two isomers giving rise to only two separate peaks.

Douek *et al.*[15] studied the far infrared spectrum of many complexes with particular emphasis on compounds of the types MX_2Q, $MX_4 \cdot 2Q$ and MX_4Q[M = Ti, Zr, Ge or Sn; X = F^-, Cl^-, Br^-, or I^-; Q = 8-quinolinol, salicylaldehyde (SalH), or acetylacetone (acacH)]. Their studies were directed to those absorptions due to vibrational modes which involve the stretching of metal–halogen bonds. Their criterion for such assignments is that an appreciable shift to lower frequencies occurs for modes of this type—designated (MX), in passing from a chloride to the analogous bromide. Those bands arising from motions involving the metal-organic ligands and vibrations within these ligands are expected to undergo only small shifts on changing the halogens. The absorption bands (450–480 cm^{-1}) of $[GeCl_2Q_2]$, $[GeBr_2Q_2]$, and $[GeI_2Q_2]$ were listed in their publication[15]. Bands at 315–340, 288 and 205 cm^{-1} are assigned to ν(M–X) modes in the chloride, bromide and iodide complexes respectively.

Again, with reference to stereochemistry, it was noted above that the single sharp carbonyl band for the EDTA complexes of germanium points strongly to a binuclear arrangement. According to Langer, three factors which have an influence on the strength of carbon–oxygen double bond are:

(1) An inductive effect increases the frequency when a nitrogen atom of EDTA is coordinated to the complex metal or when it is protonated.
(2) The nature of the asymmetric metal–acetate bond results in higher frequencies for covalent and lower frequencies for ionic bonds.
(3) Any electron withdrawing effect on the carbonyl oxygen, such as hydrogen bonding or coordination to metal, causes a lowering of the frequency.

Hence, the observed high carbonyl frequency in the spectra of the EDTA complexes[40], as well as those of the α-hydroxy acid complexes of germanium[8], leads to the assignment of binuclear structures for these complexes.

Further infrared data concerning germanium is available in the literature[4,8,15,40,56].

F. STABILITY

An excellent treatment of trends toward stability in coordination compounds of Group IV atoms is found in a review article by Gielen and Sprecher[22]. They specifically mention three major factors which influence the stability of a complex.

The nature of the metal ion—the stability of haloorganometallic complexes with nucleophilic substituents increases in the order silicon < germanium < tin.

The number of electronegative substituents—increase in stability of a complex occurs as the number of electronegative substituents directly attached to the metal increases.

The influence of the nucleophile—in general, stability of complexes, relative to the nucleophile, increases in the order $I^- < Br^- < Cl^- < F^-$.

In support of these trends, it is reported that GeF_4 forms more stable[1] complexes with cyclic ethers and Me_2O than does SiF_4. The thermal stability of the phenyl- and *p*-nitrophenylhydrazine complexes of tetravalent germanium increases in the sequence from iodide to bromide[24]. The stability of these salts, as established from the corresponding differential thermal diagrams, is greater for nitrophenylhydrazine derivatives than the phenyl derivatives. These facts are indeed in accord with the above trends, as mentioned by Gielen and Sprecher, where stability increases from silicon to germanium and from iodide to bromide.

Clerc[11] favors the stability of the *trans*-complex in preference to the *cis*-form with germanic acid. The argument lies in the more symmetrical arrangement of the substituents about the central germanium ion in the *trans*-form.

A few more specific results can be mentioned here. The formation of chelates between germanium and various 2,5-dihydroxy-*p*-benzoquinone derivatives was studied by spectrophotometry[6]. The stability of these chelates $[Ge(OH)_2R_2]^{2-}$, are linearly related to the sum of the acidity constants of the ligands. Clark noted[9] that the thio-acid complexes of germanium decompose gradually as titration with alkali proceeds beyond pH 6.0.

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