PART - A

CHAPTER - III

COMPLEXES OF SILICON (IV),
GERMANIUM (IV) AND TITANIUM (IV)
WITH QUINONE OXIMES
Introduction

Silicon, germanium, tin and titanium form number of stable complexes in their +4 oxidation state. Silicon is definitely a non-metal, germanium is a metalloid, while tin and titanium are metals.

All these elements form six coordinated octahedral and pentacoordinated trigonal bipyramidal complexes. Out of these two, octahedral is very common and important.

Till recently it is considered that silicon has no value on life science. But now silicon(IV) complexes with Schiff bases containing N' and O' donor atoms possess biological activity which might play a significant role in living organisms.

In view of the possibility of valence shell expansion by using the outer d-orbital, coordination number five and six are possible.

The solution study of 2,2'-bipyridyl complexes with tetravalent silicon, germanium and tin in acetonitrile have been reported by Tanaka et al. Kummer Dieter et al. have reported octahedral ionic complexes of the type $\text{SiCl}_2L_2^+2$, where $L = 2,2'$-bipyridine.
S.K. Dhar et al. have prepared tris(acetylacetonate) Si(IV) complex cation and have assigned asymmetric octahedral geometry. Tris-oxalato-complexes of tetravalent silicon, germanium, tin and titanium have been synthesised by P.A.W. Dean et al. and have proposed distorted octahedral geometry on the basis of infrared and Raman spectral studies.

Malhotra and his co-workers have prepared the complexes of the type MX₃L, from the metal salts MX₄, with benzoin and its derivatives (Where M = Ti, Sn and X = Cl, Br; M = Si, Zr and X = Cl). But on refluxing the solution they have obtained the complexes of the type MX₂L₂.

Pentacoordinated silicon(IV) complexes have also been reported.

The vast amount of literature added to the growth of understanding the nature of silicon-nitrogen bonds in the complexes of silicon(IV) is mainly due to Wannagal and his co-worker. Recently Paul et al. and Tandon et al. have reported few silicon(IV) complexes with nitrogen donor ligands. Mayer and co-worker have studied the thermal and semiconducting properties of Si(IV) and Ge(IV) complexes.

Von G. Schott and Karin Golz have synthesised Si(IV) complexes only with 1-nitroso-2-naphthol and 2-nitroso-1-naphthol. On the basis of elemental analysis and infrared
spectral data they have suggested $\text{SiCl}_2\text{L}_2$ composition to the complexes.

Literature survey shows that a little work has been done in the field of germanium(IV) complexes. M.S. Button and M. Webster have studied 1:1 adduct of germanium(IV) with trimethylamine and proposed pentacoordinated trigonal bi-pyramidal structure on the basis of X-ray diffraction study.

Schiff base complexes of Ge(IV) and Sn(IV) were prepared by Aggarwal and Yadav. On the basis of physico-chemical studies they have proposed in the case of Ge(IV) 1:2 adduct (Metal to ligand) having octahedral geometry, while Sn(IV) gives 1:1 as well as 1:2 adducts having octahedral geometry.

Picolines also give octahedral 1:2 adducts (metal to ligand) with germanium tetrachloride. Apart from the complexes referred above, the literature survey reveals the study of a large number of octahedral complexes of Ge(IV) and Sn(IV). Likewise hexacoordinated octahedral titanium(IV) complexes with Schiff base have been extensively studied.

Literature survey reveals that the complexes of Si(IV) and Ge(IV) are getting industrial importance during the recent years, for example in the preparation of heat sensitive recording sheet which has improved the
An insight into the literature clearly shows that there have been very few studies dwelling on the complexes of fourth group elements with benzo-quinone oximes. This observation has made the author to take up the systematic study of Si(IV), Ge(IV) and Ti(IV) complexes with quinone oximes.

Experimental

The ligands are prepared according to the procedure described in Chapter II.

Preparation of the complexes

All the operations were carried out strictly under anhydrous condition in a dry box with a continuous stream of dry nitrogen gas. The complexes were prepared as described in Chapter II.

Chemical analysis

Silicon, germanium and titanium were estimated gravimetrically and weighed as SiO₂, GeO₂ and TiO₂ respectively. The detailed procedure is given in Chapter II.

In all the complexes the chloride was estimated as
AgCl. The experimental details are given in Chapter XI.

Nitrogen, carbon and hydrogen in the complexes were estimated by microanalytical methods.

**Physical measurements**

The molar conductance values of the complexes in DMF at the concentration \( \sim 10^{-3} \text{M} \) were recorded using ELICO-CM-82 conductivity bridge, using a conductivity cell (cell constant \( = 0.58 \text{ cm}^{-1} \)).

The computerised infrared spectra of the ligands and their complexes were recorded using Perkin-Elmer model 983 instrument in the range 4000-200 cm\(^{-1}\) and Hitachi-270-30-IR spectrophotometer in the region 4000-400 cm\(^{-1}\), in KBr pallets and nujol mull.

The magnetic measurements at room temperature were made by using a Gouy balance wherein a calibrated tube for dimagnetism was used. All the complexes were found to be dimagnetic as expected.

**Results and discussion**

**Si(IV), Ge(IV) and Ti(IV) complexes with quinone oximes**

Naphthoquinone oximes, as explained earlier already were found to exist either in the quinonoid form(I) or in the benzenoid form II.
These two forms have different electronic absorption spectra. The spectrum of benzenoid form (II) is almost similar to that of naphthalene with some new bands due to localised transitions of the substituent and charge migration between the electrons of the ring and the substituent group. On the other hand, the absorption spectra of the quinonoid forms are rather broad and diffuse with no structure at all. The absorption band can be located below 300 nm. This is the region where the absorption due to $\alpha,\beta$-unsaturated ketones appears. In addition, invariably there is an absorption band located at the longer wave-length side which may be associated with $n-\pi^*$ transition. However the intensity of this band is much less compared to the short wave-length band.

$\text{1,2-Naphthoquinone-1-oxime, in ethanol and 0.1N perchloric acid - ethanol solutions, absorps at 370 nm, while}$
in 0.1N potassium hydroxide-ethanol solutions absorbs at 425 nm. In DMSO solution, it absorbs at 358 nm. In view of these observations Chatterjee has concluded that the above compound exists in quinonoid form.

Similarly, 1,2-naphthoquinone-2-oxime, in ethanol and 0.1N perchloric acid-ethanol solutions, absorbs at 370 nm and 400 nm respectively, whereas in 0.1N potassium hydroxide ethanol solution absorbs at 440 nm. In DMSO it absorbs at 390 nm, hence it exists in quinone oxime form.

In the present investigations, the electronic spectrum of the ligand reveals three bands, viz.,

i) a weak band observed around 220 nm is characteristic of $\sigma^-\sigma^*$ transition.

ii) a strong band in the region 260-280 nm is due to $\pi^-\pi^*$ transition of phenyl or naphthyl ring.

iii) a fairly strong band appearing in the region 300-390 nm (due to $n-\pi^*$ transition) which is assigned to the electronic transitions that involve changes in the vibrational energy states of the hydrogen bonded chelate rings.

The typical electronic spectra of one of the ligands
and its complex with silicon(IV) (in set) have been depicted in Fig.AIII.1.

The absence of the absorption in the region 500-800 nm may be taken for the fact that the solvent has not coordinated to the metal\textsuperscript{34}.

A comparison of the spectra of the ligands with those of the complexes leads to the conclusion that the complexes have more intense bands. This may be considered as an evidence for the complex formation.

The electronic spectra of the halogen derivatives of 1,2-naphthoquinone-1-oxime and 1,2-naphthoquinone-2-oxime 5-methoxy-o-benzoquinone-2-oxime and 5-ethoxy-o-benzoquinone-2-oxime are almost similar to those of corresponding parent ligand. Hence it is likely that these complexes also exist in quinone oxime form in the solid state as well as in solution.

Silicon(IV) quinone oxime complexes are brown to black, Ge(IV) complexes are greenish-black of black and Ti(IV) complexes are brown to reddish-brown in colour and are amorphous in nature. All the complexes are sparingly soluble in common organic solvents. Hence molecular weight determination was not possible. However the solubility of all the complexes is slightly more in DMF and DMSO.
The results of their elemental analysis Table AIII. 1-3 shows that all the complexes have 1:2 stoichiometry with general formula $\text{ML}_2\text{Cl}_2$ \footnote{where $M = \text{Si}$, \text{Ge} and \text{Ti}; LH = ligand, i.e. one of the quinone oximes).}

**Conductance**

The conductance values of the complexes are too low to account for any electrolytic dissociation in DMF. Hence all the complexes are regarded as non-electrolytes.

It has been clearly pointed out in Chapter I that various o-nitroso-phenols and naphthols and their complexes exist in quinone oxime form in the solid state. Therefore a more appropriate method of naming these compounds would be:

1-nitroso-2-naphthol is named as 1,2-naphthoquinone-1-oxime and 2-nitroso-1-naphthol as 1,2-naphthoquinone-2-oxime. Similarly the complexes of Si(IV) with the above ligands are named as $\text{Dichloro bis(1,2-naphthoquinone-2-oximato) Si(IV)}$ and $\text{Dichloro bis(1,2-naphthoquinone-2-oximato) Si(IV)}$ respectively. In the similar way, Ge(IV) and Ti(IV) complexes can be named.

The important infrared frequencies of the ligands and Si(IV), Ge(IV) and Ti(IV) complexes and their assignments are listed in Table AIII.4-7. The typical spectra of the
The work so far reported on o-nitroso-phenols is mainly concerned with the assignments of coordination sites with the help of X-ray and spectral studies. Regarding the coordination mode of these ligands different opinions have been expressed. Even though, it is now fairly well established that these ligands form $M$ and $O$ chelates containing five membered rings. We have assigned the important infrared frequencies of the ligands and their complexes in support of the earlier assignments.

1) 1,2-Naphthoquinone-1-oxime

Of this ligand, the characteristic frequencies can be expected in the region:

i) 3800-2400 cm$^{-1}$
ii) 1700-1500 cm$^{-1}$ and
iii) 1250-1000 cm$^{-1}$.

i) The region 3800-2400 cm$^{-1}$

Intramolecular hydrogen bonding can be expected irrespective of whether the ligand has the benzenoid structure or quinone-oxime structure. It is observed that, the mull
spectrum of the ligand does not show the O-H stretching frequency. Amstutz et al.\textsuperscript{37} Gurrieri and Siracusa\textsuperscript{30} and Boli\textsuperscript{38} have also failed to notice any band in this region of the spectrum.

Hadzi\textsuperscript{39} reported a very weak and broad band of medium intensity centred around 2700 cm\textsuperscript{-1} can only be observed if sufficient thick layer of solid or saturated solution in carbon tetrachloride is used. This is attributed to a strong intra-molecular hydrogen bonding in 1,2-naphthoquinone-1-oxime\textsuperscript{40}. This is the conclusive evidence to show that there is no free hydroxyl group in this molecule.

ii) The region 1700-1500 cm\textsuperscript{-1}

In this region, absorption due to \textsuperscript{\textsuperscript{-\textsuperscript{\equiv}C=O}}, \textsuperscript{\textsuperscript{-\textsuperscript{(\equiv}C=N)} and \textsuperscript{\textsuperscript{-\textsuperscript{\equiv}N=O}} usually appear. The spectrum of the ligand shows a band around 1625 cm\textsuperscript{-1} having weak shoulders at 1659 cm\textsuperscript{-1}, 1617 cm\textsuperscript{-1}, 1596 cm\textsuperscript{-1}, 1568 cm\textsuperscript{-1} and 1535 cm\textsuperscript{-1}. There is a controversy in respect of the assignments of these frequencies. Hadzi\textsuperscript{39}, Janowski and Cuckrowski\textsuperscript{41} attributed 1629 cm\textsuperscript{-1} to \textsuperscript{\textsuperscript{-\textsuperscript{\equiv}C=O}} and 1568 cm\textsuperscript{-1} to \textsuperscript{\textsuperscript{-\textsuperscript{(\equiv}C=N)} absorptions. On the other hand, Gurrieri and Siracusa\textsuperscript{30} report that \textsuperscript{\textsuperscript{-\textsuperscript{\equiv}C=O}} band appears at 1617 cm\textsuperscript{-1} and that of \textsuperscript{\textsuperscript{-\textsuperscript{(\equiv}C=N)} band at 1659 cm\textsuperscript{-1}. In view of this ambiguity, we have compared the spectrum of 1,2-naphthoquinone-1-oxime with that of 2-naphthol. The spectrum of
2-naphthol displays two strong bands; one at 1617 cm\(^{-1}\) and the other at 1535 cm\(^{-1}\). These are due to C=C skeletal in-plane modes. The absorption at 1659 cm\(^{-1}\) assigned by Gurrieri and Siracusa to \(\nu(C=N)\) is very weak; hence it could be either due to an overtone or a combination band. Further, 1659 cm\(^{-1}\) band was not observed in this region at all in the spectra of the complexes. Moreover, Gurrieri and Siracusa found a shift of nearly 180 cm\(^{-1}\) of this frequency (1659 cm\(^{-1}\)) on complex formation, which is unlikely. Hence the assignment of this frequency to \(\nu(C=N)\) is not reasonable. In the light of this, a stronger band at 1625 cm\(^{-1}\) and a weaker band at 1565 cm\(^{-1}\) which we have assigned is in agreement with Janowski and Cuckrowski to \(\nu(C=O)\) and \(\nu(C=N)\) respectively. Because, usually a strong band is expected for \(\nu(C=O)\) and a low intensity band is expected for the \(\nu(C=N)\) vibrations.

Generally, aromatic nitroso compounds have the N=O absorption around 1500 cm\(^{-1}\). But the spectrum of 1,2-naphthoquinone-1-oxime does not display any band in this region attributable to \(\nu(N=O)\).

iii) The region 1250-1000 cm\(^{-1}\)

The spectra in this region strongly suggest the quinone-oxime form for the ligand.
According to Janowski et al.\textsuperscript{41} in simple oximes, the N-O stretching frequency lies in the range 930-960 cm\textsuperscript{-1}. The same frequency in quinone-monoximes was observed by Gurrieri et al.\textsuperscript{30} and Palm et al.\textsuperscript{42,43} between 980-1080 cm\textsuperscript{-1}. This is attributed to the resonance between the structures A and B.

\[
\begin{align*}
\text{A} & \quad \text{B} \\
\text{NOH} & \quad \text{N=OH} \\
\end{align*}
\]

The presence of a sharp band around 1080 cm\textsuperscript{-1}, assignable to \(\text{\textgamma} (\text{N-O})\) in the spectrum of 1,2-naphthoquinone-1-oxime is in support of its quinone-oxime structure. This frequency is not observed in the spectrum of 2-naphthol. This observation agrees very well with the earlier reports\textsuperscript{30,39}.

The chloro- and bromo- substitution on 1,2-naphthoquinone-1-oxime molecule does not alter appreciably the infrared frequencies of the intra-molecular hydrogen bonded \(-\text{CH}, \text{\textgamma} (\text{C=O}), \text{\textgamma} (\text{C=N})\) and \(\text{\textgamma} (\text{N-O})\) groups. Hence it may safely
be assumed that the above halogen derivatives of this ligand also exist in quinone oxime form.

2) 1,2-Naphthoquinone-2-oxime

The infrared spectrum of 1,2-naphthoquinone-2-oxime in mull has a broad band centred around 3259 cm\(^{-1}\) due to intramolecular hydrogen bonded O-H. This low value is caused by intra-molecular association. In the region 1700-1500 cm\(^{-1}\) four absorption bands are observed at 1676 cm\(^{-1}\), 1624 cm\(^{-1}\), 1600 cm\(^{-1}\) and 1560 cm\(^{-1}\). Here also there is a controversy on the assignment of the frequencies. The strong band at 1676 cm\(^{-1}\) is assigned to \(\nu (C=O)\) and there is uniform agreement. The bands at 1625 cm\(^{-1}\) and 1600 cm\(^{-1}\) are due to C=C as in the case of 1,2-naphthoquinone-1-oxime. Hadzi\(^{39}\) has assigned 1557 cm\(^{-1}\) band to \(\nu (C=N)\) which was found at 1645 cm\(^{-1}\). But by analogy to 1,2-naphthoquinone-1-oxime \(\Gamma \nu (C=N) = 1568\) cm\(^{-1}\), we have assigned 1560 cm\(^{-1}\).
band to \( \nu (C=\text{N}) \) frequency and agree with the assignment of Hadzi\textsuperscript{39}.

In the lower region Gurrieri and Siracusa\textsuperscript{30} have assigned a band at 935 cm\textsuperscript{-1} to \( \nu (N-O) \) absorption. But this is controversy to the general observation that the quinone oximes have \( \nu (N-O) \) stretching frequency in the region 980-1080 cm\textsuperscript{-1}. Simple oximes are known to exhibit \( \nu (N-O) \) absorption around 935 cm\textsuperscript{-1}. However, Hadzi\textsuperscript{39} attributes a band at 1075 cm\textsuperscript{-1} to \( \nu (N-O) \) and our observation \( \nu (N-O) = 1078 \text{ cm}^{-1} \) agrees very well with this assignment.

X-Ray crystallographic study of 5-methoxy-\( \alpha \)-benzquinone-2-oxime and 5-ethoxy-\( \alpha \)-benzoquinone-2-oxime have revealed the quinone oxime structure for these molecule as suggested by Bartindale et al.\textsuperscript{44}

**Infrared spectra of Si(IV), Ge(IV) and Ti(IV) complexes**

The typical infrared spectra of the complexes are depicted in Figs. AIII-(4-9) important infrared bands and their assignments are listed in Table AIII-5-7.

It has been concluded from the infrared spectral evidences that the benzo and naphthoquinone oximes exist in the quinone oxime form in the solid state.
The region 3800-2400 cm\(^{-1}\)

A broad band around 3200 cm\(^{-1}\) assignable to intramolecular hydrogen bonded hydroxyl group observed in the spectra of the ligands is missing in the spectra of the complexes. This indicates that the hydrogen atom of the oximic group has been replaced by the metal ion.

The region 1700-1500 cm\(^{-1}\)

The spectra of all the complexes show bands around 1625-1610 cm\(^{-1}\) and around 1570-1550 cm\(^{-1}\). The former one is assigned to \(\gamma\) (C=O) stretching frequency and the latter one is assigned to \(\gamma\) (C=N) stretching frequency. On comparing these bands with the bands observed in the ligand spectrum, we notice that \(\gamma\) (C=O) and \(\gamma\) (C=N) stretching frequencies show red shift. This shows the probable coordination through carbonyl oxygen and nitrogen of oximic group. As reasoned before, in the case of the ligands there is no absorption that can be attributed to \(\gamma\) (N=O).

In all the spectra, the other bands that need attention are between 1500-1400 cm\(^{-1}\). These are due to C=C and benzenoid vibrations.
The region 1250-1000 cm\(^{-1}\)

In the spectra of the complexes the frequencies pertaining to \(\nu(N-O)\) is noticed around 1090-1070 cm\(^{-1}\). On comparison with the ligand spectrum, it is observed that N-O stretching frequency has experienced a blue shift upon complexation.

The above frequency shift indicates that the present complexes in the solid state have the quinone oxime structure i.e., structure (I) is converted into structure (II) on complexation.

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\begin{array}{c}
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{O} \\
\text{H}
\end{array} \\
\text{X}
\end{array} & \quad \begin{array}{c}
\begin{array}{c}
\text{N} \\
\text{Cl} \\
\text{Si}_2
\end{array} \\
\text{X}
\end{array}
\end{align*}
\]

(Where X = H, Cl and Br).

This results in the lengthening of the C=O and C=N bonds and shortening of the N=O bond. Hence all the above
observations collectively support the conclusion that the ligands under present study utilise the oximic nitrogen and the carbonyl oxygen as the coordinating sites and form five membered chelates.

The metal ligand and metal chloride related vibrations are known to occur in the lower region between 1000-300 cm\(^{-1}\). The spectra of the silicon(IV) complexes under study manifest three more new bands which are absent in the ligands. Of the three bands observed, the one that appeared around 980-970 cm\(^{-1}\) may be assigned to \(\nu(Si-O)\) which is in agreement with Gupta et al. The second band observed around 740-720 cm\(^{-1}\) may be assigned to \(\nu(Si-N)\). Finally, the one that appeared around 480-475 cm\(^{-1}\) may be attributed to \(\nu(Si-Cl)\) stretching frequency.

Like silicon, the germanium(IV) complexes also exhibit three new bands which are absent in the spectra of ligands. The band observed around 665-645 cm\(^{-1}\) can be assigned to \(\nu(Ge-N)\), stretching frequency which is in line with E. M. Belousova et al. and others. The one that observed around 550-540 cm\(^{-1}\) is attributed to \(\nu(Ge-O)\) stretching frequency, which is in close agreement with a previous assignments. Lastly 360-340 cm\(^{-1}\) band may be assigned to \(\nu(Ge-Cl)\).
In the case of Ti(IV) complexes, these bands are observed around 560-520 cm$^{-1}$, 470-415 cm$^{-1}$ and around 350 cm$^{-1}$ and have been assigned to $\tilde{\gamma}$(Ti-N), $\tilde{\gamma}$(Ti-O) and $\tilde{\gamma}$(Ti-Cl) stretching frequencies respectively, which are in close agreement with previous assignments$^{48-52}$.

The spectral evidences, analytical data and conductivity measurements suggest that Si(IV), Ge(IV) and Ti(IV) exhibit coordination number six in all these complexes. Tentatively, the following structure may be proposed for the above complexes.

\[
\begin{array}{c}
\text{Cl} \\
\text{M} \\
\text{Cl} \\
\text{N} \\
\text{O} \\
\text{O} \\
\end{array}
\]

where \( M = \text{Si(IV)}, \text{Ge(IV)} \) and \( \text{Ti(IV)} \).
Summary

Silicon(IV), Ge(IV) and Ti(IV) complexes with quinone oximes have been prepared by reacting corresponding metal tetrachlorides with quinone oximes in the ratio of 1:2 (metal to ligand) in dry benzene medium. The complexes were characterised by analytical and spectral data. These complexes were found to be non-electrolytes in DMF and appear to have coordination number six.
Table AIII.1
Analytical Data of silicon(IV) complexes with quinone oximes

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complex</th>
<th>% Metal</th>
<th>% Carbon</th>
<th>% Hydrogen</th>
<th>% Nitrogen</th>
<th>% Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{Si}(\text{C}<em>{10}\text{H}</em>{6}\text{NO}_2)_2\text{Cl}_2^-$</td>
<td>6.32</td>
<td>6.41</td>
<td>54.19</td>
<td>54.30</td>
<td>2.71</td>
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<tr>
<td>2</td>
<td>$\text{Si}(\text{C}_{10}\text{H}_5\text{NO}_2\text{Cl})_2\text{Cl}_2^-$</td>
<td>5.46</td>
<td>5.50</td>
<td>46.87</td>
<td>47.00</td>
<td>1.95</td>
</tr>
<tr>
<td>3</td>
<td>$\text{Si}(\text{C}_{10}\text{H}_5\text{NO}_2\text{Br})_2\text{Cl}_2^-$</td>
<td>4.68</td>
<td>4.59</td>
<td>39.93</td>
<td>39.79</td>
<td>1.66</td>
</tr>
<tr>
<td>4</td>
<td>$\text{Si}(\text{C}_{10}\text{H}_6\text{NO}_2)_2\text{Cl}_2^-$</td>
<td>6.32</td>
<td>6.45</td>
<td>54.19</td>
<td>54.40</td>
<td>2.71</td>
</tr>
<tr>
<td>5</td>
<td>$\text{Si}(\text{C}_{7}\text{H}_6\text{NO}_3)_2\text{Cl}_2^-$</td>
<td>6.95</td>
<td>6.83</td>
<td>41.69</td>
<td>41.58</td>
<td>2.98</td>
</tr>
<tr>
<td>6</td>
<td>$\text{Si}(\text{C}_8\text{H}_8\text{NO}_3)_2\text{Cl}_2^-$</td>
<td>6.50</td>
<td>6.61</td>
<td>44.54</td>
<td>44.50</td>
<td>3.79</td>
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Table AIII.2
Analytical data of titanium(IV) complexes with quinone oximes

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<th>S. No.</th>
<th>Complex</th>
<th>% Metal</th>
<th>% Carbon</th>
<th>% Hydrogen</th>
<th>% Nitrogen</th>
<th>% Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{Ti(C}_{10}\text{H}_6\text{NO}_2\text{)}_2\text{Cl}_2$</td>
<td>10.35</td>
<td>51.85</td>
<td>2.59</td>
<td>6.05</td>
<td>15.34</td>
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<td></td>
<td></td>
<td>10.42</td>
<td>51.72</td>
<td>2.56</td>
<td>6.15</td>
<td>15.42</td>
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<tr>
<td>2</td>
<td>$\text{Ti(C}_{10}\text{H}_5\text{NO}_2\text{Cl}}_2\text{Cl}_2$</td>
<td>9.00</td>
<td>45.12</td>
<td>1.88</td>
<td>5.26</td>
<td>26.69</td>
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<td></td>
<td></td>
<td>9.12</td>
<td>45.38</td>
<td>1.85</td>
<td>5.20</td>
<td>26.74</td>
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<tr>
<td>3</td>
<td>$\text{Ti(C}_{10}\text{H}_5\text{NO}_2\text{Br}}_2\text{Cl}_2$</td>
<td>7.64</td>
<td>38.53</td>
<td>1.61</td>
<td>4.49</td>
<td>11.39</td>
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<td></td>
<td></td>
<td>7.61</td>
<td>38.40</td>
<td>1.59</td>
<td>4.51</td>
<td>11.44</td>
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<td>4</td>
<td>$\text{Ti(C}_{10}\text{H}_6\text{NO}_2\text{)}_2\text{Cl}_2$</td>
<td>10.35</td>
<td>51.85</td>
<td>2.59</td>
<td>6.05</td>
<td>15.34</td>
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<td></td>
<td></td>
<td>10.40</td>
<td>51.80</td>
<td>2.54</td>
<td>6.11</td>
<td>15.46</td>
</tr>
<tr>
<td>5</td>
<td>$\text{Ti(C}_{7}\text{H}_6\text{NO}_3\text{)}_2\text{Cl}_2$</td>
<td>11.33</td>
<td>39.73</td>
<td>2.84</td>
<td>6.62</td>
<td>16.79</td>
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<td></td>
<td></td>
<td>11.45</td>
<td>39.58</td>
<td>2.81</td>
<td>6.56</td>
<td>16.86</td>
</tr>
<tr>
<td>6</td>
<td>$\text{Ti(C}_{8}\text{H}_8\text{NO}_3\text{)}_2\text{Cl}_2$</td>
<td>-10.62</td>
<td>42.58</td>
<td>3.55</td>
<td>6.21</td>
<td>15.75</td>
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<td></td>
<td></td>
<td>-10.54</td>
<td>42.45</td>
<td>3.52</td>
<td>6.14</td>
<td>15.90</td>
</tr>
</tbody>
</table>
Table AIII.3
Analytical data of germanium(IV) complexes with quinone oximes

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complex</th>
<th>% Metal Expt.</th>
<th>% Carbon Expt.</th>
<th>% Carbon Found</th>
<th>% Hydrogen Expt.</th>
<th>% Hydrogen Found</th>
<th>% Nitrogen Expt.</th>
<th>% Nitrogen Found</th>
<th>% Chloride Expt.</th>
<th>% Chloride Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ge(C_{10}H_{8}NO_{2})<em>{2}Cl</em>{2}</td>
<td>14.88</td>
<td>49.22</td>
<td>48.63</td>
<td>2.46</td>
<td>2.42</td>
<td>5.74</td>
<td>5.62</td>
<td>14.56</td>
<td>14.38</td>
</tr>
<tr>
<td>2</td>
<td>Ge(C_{10}H_{5}NO_{2}Cl)<em>{2}Cl</em>{2}</td>
<td>13.01</td>
<td>43.04</td>
<td>42.55</td>
<td>1.79</td>
<td>1.76</td>
<td>5.02</td>
<td>4.92</td>
<td>25.46</td>
<td>26.01</td>
</tr>
<tr>
<td>3</td>
<td>Ge(C_{10}H_{5}NO_{2}Br)<em>{2}Cl</em>{2}</td>
<td>11.23</td>
<td>37.12</td>
<td>37.31</td>
<td>1.54</td>
<td>1.52</td>
<td>4.33</td>
<td>4.29</td>
<td>10.98</td>
<td>11.20</td>
</tr>
<tr>
<td>4</td>
<td>Ge(C_{10}H_{6}NO_{2})<em>{2}Cl</em>{2}</td>
<td>14.88</td>
<td>49.22</td>
<td>48.80</td>
<td>2.46</td>
<td>2.50</td>
<td>5.74</td>
<td>5.63</td>
<td>14.56</td>
<td>14.32</td>
</tr>
<tr>
<td>5</td>
<td>Ge(C_{7}H_{6}NO_{3})<em>{2}Cl</em>{2}</td>
<td>16.22</td>
<td>37.53</td>
<td>37.12</td>
<td>2.68</td>
<td>2.70</td>
<td>6.26</td>
<td>6.18</td>
<td>15.86</td>
<td>15.95</td>
</tr>
<tr>
<td>6</td>
<td>Ge(C_{8}H_{8}NO_{3})<em>{2}Cl</em>{2}</td>
<td>15.26</td>
<td>40.37</td>
<td>39.86</td>
<td>3.36</td>
<td>3.32</td>
<td>5.88</td>
<td>5.81</td>
<td>14.93</td>
<td>15.02</td>
</tr>
</tbody>
</table>
Table AIII.4

Important infrared bands of the ligands and their assignments (cm\(^{-1}\))

<table>
<thead>
<tr>
<th></th>
<th>1,2-Naphthoquinone-1-oxime</th>
<th>3-Chloro-1,2-naphthoquinone-1-oxime</th>
<th>3-Bromo-1,2-naphthoquinone-1-oxime</th>
<th>1,2-Naphthoquinone-2-oxime</th>
<th>5-Methoxy- o-benzoquinone-2-oxime</th>
<th>5-Ethoxy- o-benzoquinone-2-oxime</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1625s</td>
<td>1625m</td>
<td>1618s</td>
<td>1622s</td>
<td>1655w</td>
<td>1650m</td>
<td>(\gamma) (C=O)</td>
<td></td>
</tr>
<tr>
<td>1570s</td>
<td>1565m</td>
<td>1565m</td>
<td>1562s</td>
<td>1555m</td>
<td>1550m</td>
<td>(\gamma) (C=N)</td>
<td></td>
</tr>
<tr>
<td>1070vs</td>
<td>1075s</td>
<td>1075s</td>
<td>1078s</td>
<td>1055s</td>
<td>1060s</td>
<td>(\gamma) (N=O)</td>
<td></td>
</tr>
</tbody>
</table>

vs - very sharp; m - medium; w - weak
**Table AIII.5**

Important infrared bands of silicon(IV) complexes and their assignments (cm⁻¹)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complex</th>
<th>v(C=O)</th>
<th>v(C=N)</th>
<th>v(N-O)</th>
<th>v(M-O)</th>
<th>v(M-N)</th>
<th>v(M-Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[^{\text{Dichloro bis(1,2-naphtho-}}\text{quinone-1-oximato)}\text{Si(IV)}]</td>
<td>1605s</td>
<td>1545s</td>
<td>1095m</td>
<td>980m</td>
<td>740m</td>
<td>475m</td>
</tr>
<tr>
<td>2</td>
<td>[^{\text{Dichloro bis(3-chloro-1,2-naphthoquinone-1-oximato)}\text{-Si(IV)}]</td>
<td>1605s</td>
<td>1550s</td>
<td>1098s</td>
<td>970m</td>
<td>740s</td>
<td>478m</td>
</tr>
<tr>
<td>3</td>
<td>[^{\text{Dichloro bis(3-bromo-1,2-naphthoquinone-1-oximato)}\text{-Si(IV)}]</td>
<td>1603s</td>
<td>1548s</td>
<td>1105s</td>
<td>972m</td>
<td>745s</td>
<td>480w</td>
</tr>
<tr>
<td>4</td>
<td>[^{\text{Dichloro bis(1,2-naphtho-}}\text{quinone-2-oximato)}\text{Si(IV)}]</td>
<td>1600s</td>
<td>1544s</td>
<td>1090m</td>
<td>970s</td>
<td>720m</td>
<td>480w</td>
</tr>
<tr>
<td>5</td>
<td>[^{\text{Dichloro bis(5-methoxy-o-}}\text{Benzoquinone-2-oximato)}\text{Si(IV)}]</td>
<td>1630m</td>
<td>1530m</td>
<td>1070m</td>
<td>967w</td>
<td>735w</td>
<td>482w</td>
</tr>
<tr>
<td>6</td>
<td>[^{\text{Dichloro bis(5-ethoxy-o-benzo-}}\text{quinone-2-oximato)}\text{Si(IV)}]</td>
<td>1610m</td>
<td>1520m</td>
<td>1080s</td>
<td>980m</td>
<td>740w</td>
<td>475s</td>
</tr>
</tbody>
</table>

s - sharp; m - medium; w - weak
### Important infrared bands of titanium(IV) complexes and their assignments (cm⁻¹)

<table>
<thead>
<tr>
<th>No.</th>
<th>Complex</th>
<th>(cm⁻¹)</th>
<th>(w-Cl)</th>
<th>(w-O)</th>
<th>(M-O)</th>
<th>(M=O)</th>
<th>(C=O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dichloro bis(1,2-naphthoquinone-1-oximato)Ti(IV)</td>
<td>1608s</td>
<td>1552m</td>
<td>1102m</td>
<td>1080m</td>
<td>440m</td>
<td>520s</td>
</tr>
<tr>
<td>2</td>
<td>Dichloro bis(3-chloro-1,2-naphthoquinone-1-oximato)Ti(IV)</td>
<td>1600s</td>
<td>1560s</td>
<td>1080m</td>
<td>1108s</td>
<td>452W</td>
<td>558m</td>
</tr>
<tr>
<td>3</td>
<td>Dichloro bis(3-bromo-1,2-naphthoquinone-1-oximato)Ti(IV)</td>
<td>1616s</td>
<td>1558s</td>
<td>1108s</td>
<td>1100m</td>
<td>458m</td>
<td>562m</td>
</tr>
<tr>
<td>4</td>
<td>Dichloro bis(5-methoxy-o-benzoquinone-2-oximato)Ti(IV)</td>
<td>1612s</td>
<td>1555s</td>
<td>1100m</td>
<td>1105m</td>
<td>522W</td>
<td>540m</td>
</tr>
<tr>
<td>5</td>
<td>Dichloro bis(5-ethoxy-o-benzoquinone-2-oximato)Ti(IV)</td>
<td>1606s</td>
<td>1536m</td>
<td>1110m</td>
<td>1110m</td>
<td>440s</td>
<td>538m</td>
</tr>
<tr>
<td>6</td>
<td>Dichloro bis(1,2-naphthoquinone-1-oximato)Ti(IV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- s = sharp; m = medium; w = weak
Table AIII.7
Important infrared bands of germanium(IV) complexes and their assignments (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complex</th>
<th>(\nu) (C=O)</th>
<th>(\nu) (C=N)</th>
<th>(\nu) (N-O)</th>
<th>(\nu) (M-O)</th>
<th>(\nu) (M-N)</th>
<th>(\nu) (M-Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dichloro bis(1,2-naphthoquinone-1-oximato)Ge(IV)(^{7})</td>
<td>1600s</td>
<td>1554m</td>
<td>1080s</td>
<td>550m</td>
<td>665s</td>
<td>360m</td>
</tr>
<tr>
<td>2</td>
<td>Dichloro bis(3-chloro-1,2-naphthoquinone-1-oximato)Ge(IV)(^{7})</td>
<td>1598s</td>
<td>1540s</td>
<td>1082m</td>
<td>550m</td>
<td>645s</td>
<td>355w</td>
</tr>
<tr>
<td>3</td>
<td>Dichloro bis(3-bromo-1,2-naphthoquinone-1-oximato)Ge(IV)(^{7})</td>
<td>1608s</td>
<td>1532s</td>
<td>1080m</td>
<td>555s</td>
<td>660s</td>
<td>345w</td>
</tr>
<tr>
<td>4</td>
<td>Dichloro bis(1,2-naphthoquinone-2-oximato)Ge(IV)(^{7})</td>
<td>1605s</td>
<td>1525m</td>
<td>1088m</td>
<td>540m</td>
<td>665s</td>
<td>355m</td>
</tr>
<tr>
<td>5</td>
<td>Dichloro bis(5-methoxy-o-benzoquinone-2-oximato)Ge(IV)(^{7})</td>
<td>1610s</td>
<td>1538s</td>
<td>1095s</td>
<td>540m</td>
<td>658m</td>
<td>340w</td>
</tr>
<tr>
<td>6</td>
<td>Dichloro bis(5-ethoxy-o-benzoquinone-2-oximato)Ge(IV)(^{7})</td>
<td>1608s</td>
<td>1540s</td>
<td>1100m</td>
<td>545m</td>
<td>660m</td>
<td>345m</td>
</tr>
</tbody>
</table>

s = sharp; m = medium; w = weak
1,2-NAPHTHOQUINONE-1-OXIME
[ Dichloro-bis(1,2-Naphtoquinone - Oximato) Si(IV) ]

ABSORBANCE

WAVELENGTH (nm)
5-ETHOXY-o-BENZQUINONE-2-OXIME

TRANSMISSION (%)
DICHLOORO BIS(1, 2-NAPHTHOQUINONE-1-OXIMATO) SI(IV)

TRANSMISSION (%)
DICHLOORO BIS (5-ETHOXY-6-BENZOQUINEONE-2-OXIMATO) SI(IV)

TRANSMISSION (%)
DICHLOOROBIS (1, 2-NAPHTHOQUINONE-1-OXIMATO) Ge(IV)

TRANSMISSION (%)

WAVELENGTH (CM$^{-1}$)

Fig. A.III.6.
DICHLOORO BIS (5-ETHOXY-o-BENZOQUINONE-2-OXIMATO) Ge(IV)
Dichloro bis(1,2-naphthoquinone-1-oximato) Ti(IV)

Fig. A III. 8.
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