

EXTENDED CO-ORDINATION THEORY OF VALENCY. II.

Configuration of Carbon Compounds.

By RYUTARO TSUCHIDA.

Introduction.

The co-ordination theory of Werner has proved far-reaching in its scope and has been fully substantiated by both chemical and physical evidence. The present paper is a continuation of the article¹⁾ on the same subject which deals with an extension of the co-ordination theory to simple ions and molecules by assuming that all the chemical bonds are co-ordinate links. The covalent and the co-ordinate links are usually treated discriminatingly, in spite of ample evidence revealing that there is no essential difference between these bonds. Apparent differences are: (1) the manner of bond-formation, (2) the relation between the bond and the valency, and (3) the directional tendency of bonds. For the purpose of unitary treatment of the simple and the complex compound, it is first necessary to explain the apparent differences between these two kinds of links. In the covalent link the bond-electrons are furnished by both the atoms to combine, whereas in the co-ordinate link the electrons are donated only by the ligand, i.e., the co-ordinated ion or molecule. For example, the covalent bond in carbon tetrachloride is formed by the electrons given by the carbon and the chlorine atom, whereas the electrons of the co-ordinate link in $[\text{SnCl}_6]^-$ are furnished only by the chlorine ion as ligand. This difference in the manner of bond formation can be easily removed by simply assuming that all the compounds are built up by co-ordinating ligands around central cations. For example, carbon tetrachloride is assumed to form the molecule by co-ordinating four chlorine anions around a quadrivalent carbon cation. Then the simple molecule could be treated just as the complex compound. The second difference between the covalent and the co-ordinate compound is that the valency coincides with the number of bonds in the former, but generally not in the latter. For instance the carbon atom in carbon tetrachloride is quadrivalent and has four bonds, while the boron atom in fluoroborate ion is trivalent, but has four bonds. By the above

1) R. Tsuchida, *Bull. Chem. Soc. Japan*, 14, 101 (1939); *J. Chem. Soc. Japan*, 60, 245 (1939).

assumption, the links in CCl_4 as well as in $[\text{BF}_4]^-$ are all co-ordinate bonds. The bond is, therefore, a formal expression of the co-ordinate link and consequently the number of bonds coincides with the co-ordination number. On the contrary, the valency does not necessarily coincide with the number of bonds. It can be seen by the following consideration that there is no relation between the valency and the number of bonds. We know that the same center can have different number of bonds. For example cupric ion can have three, four and six bonds in $[\text{CuCl}_2]^-$, $[\text{Cu}(\text{OH}_2)_4]^{++}$ and $[\text{Cu}(\text{NH}_3)_6]^{++}$ respectively. Moreover, the electrovalence can not be shown by the bond, but nevertheless the element in the electrovalent compound has the valency represented by the charge of the ion. In special cases the valency may coincide with the number of bonds as well as the co-ordination number, e.g., in carbon tetrachloride, ammonia, water, etc. It should be noticed, however, that such coincidence is not always expected for all the neutral molecules. For instance, tervalent cobaltic ion has six bonds in the neutral molecule of $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$. Another difference between the covalent and the co-ordinate link is concerned with the direction of bonds. It is well established that the ligands are symmetrically co-ordinated around the central atom, and the configuration of the complex ion or molecule is linear, trigonal, etc. according as the co-ordination number is two, three, etc. as is shown in Table I.

Table I.

Co-ordination number	Configuration	Example
2	linear	$[\text{Ag}(\text{CN})_2]^-$
3	planar triangle	$[\text{CuCl}_3]^-$
4	tetrahedron	$[\text{Zn}(\text{NH}_3)_4]^{++}$
4	planar square	$[\text{Cu}(\text{NH}_3)_4]^{++}$
6	octahedron	$[\text{PtCl}_6]^-$

On the other hand, some simple compounds have apparently special valence-angles. For examples, the water molecule is V-shaped, the angle $\angle \text{HOH}$ being 105° and the ammonia molecule is pyramidal, the angle $\angle \text{HNH}$ being 106° . Thus the covalent bond seems to have valence-bonds in some fixed directions, whereas the co-ordination compound has symmetrically distributed bonds as is shown above. From the viewpoint that all the ions and molecules are built up by co-ordination, however, the molecules of water, ammonia, etc. could not be exempted from the general rule of symmetrical co-ordination. Explanation for such anomalous valence-angles is, therefore, required. The electronic configura-

tion of the nitrogen atom in its ground state is $1s^2, 2s^2, 2p_x, 2p_y, 2p_z$. Pauling²⁾ assumed that s^2 -electrons have no effect on the combination with other atoms by p -electrons and derived the valence-angle of 90° . In the present method, however, the effect of $2s^2$ -electrons is taken into consideration by the following simple method. Three hydrogen anions and a pair of electrons are assumed to co-ordinate around a quinquevalent nitrogen cation. It is postulated that such a pair of electrons has approximately the same share as other ligands in co-ordination. Then these four ligands, the three hydrogen anions and the pair of electrons, are co-ordinated tetrahedrally in accordance with the general rule of symmetrical co-ordination. Thus the resulting molecule of ammonia has a pyramidal configuration, the angle $\angle \text{HNH}$ being 109° in a fair coincidence with the experimental result of 106° . Similarly a sexavalent oxygen cation is the co-ordination center and two hydrogen anions and two pairs of electrons are the ligands in the molecule of water. The resulting molecule is V-shaped, the angle $\angle \text{HOH}$ being 109° for the observed value of 105° . In the preceding papers,¹⁾ configuration of a number of compounds has been discussed by the present method of co-ordination. In Table II are tabulated the theoretical results which coincide with experimental data without serious discrepancy.

Table II.

Ions and molecules	Configuration
$\text{BeO}_2^=, \text{BO}_2^-, [\text{Ag}(\text{CN})_2]^-, \text{Zn}(\text{C}_2\text{H}_3)_2, \text{CH}_3\text{MgI}, \text{etc.}$	linear
$\text{H}_2\text{O}, \text{etc.}$	V-shaped (109°)
$\text{NO}_2, \text{NO}_2^-, \text{SO}_2, \text{etc.}$	V-shaped (120°)
$\text{BCl}_3, \text{NO}_3^-, \text{SO}_3, [\text{Ni}(\text{CN})_3]^=, \text{etc.}$	plane-triangle
$\text{SO}_3^=, \text{ClO}_3^-, \text{NH}_3, \text{etc.}$	pyramidal (109°)
$[\text{PtCl}_4]^=, [\text{Pt}(\text{NH}_3)_4]^{++}, \text{dimethylglyoximonickel}, \text{etc.}$	plane-tetragonal
$\text{PO}_4^=, \text{SO}_4^=, \text{ClO}_4^-, \text{NH}_4^+, \text{CrO}_4^=, \text{MnO}_4^-, \text{MnO}_4^=, \text{Ni}(\text{CO})_4, \text{SnBr}_4, \text{Pt}(\text{C}_2\text{H}_5)_4, [\text{Cu}(\text{CN})_4]^=, [\text{Zn}(\text{NH}_3)_4]^{++}, \text{etc.}$	tetrahedral
$\text{SF}_6, \text{IO}_6^{5-}, [\text{PtCl}_6]^=, [\text{Fe}(\text{CN})_6]^=, [\text{NbF}_5\text{O}]^=, [\text{Cr}(\text{H}_2\text{O})_6]^{+++}, \text{etc.}$	octahedral
$\text{OsF}_8, [\text{W}(\text{CN})_6]^=, [\text{Ni}(\text{NH}_3)_6]^{++}, \text{etc.}$	cubic

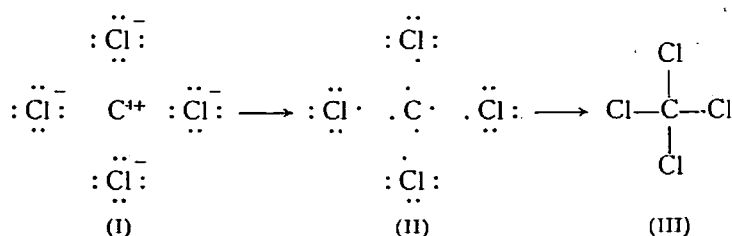
In the present paper the configuration of carbon compounds will be discussed. As has been stated in the previous papers, the co-ordination number of carbon can not exceed four, only four wave-functions, $2s, 2p_x, 2p_y$, and $2p_z$, being available for co-ordination. In carbon compounds, therefore, one, two, three or four ligands are co-ordinated around quadrivalent carbon cations, the resulting configuration being linear, trigonal or tetrahedral. These configurations will be dealt

2) L. Pauling, *J. Am. Chem. Soc.*, **53**, 1367 (1931).

with in order and the nature of the aromatic, the 'double' and the 'triple' bonds will also be considered.

Tetrahedral Configuration.

The co-ordination process in carbon compounds may be assumed to take place in the following scheme. By analogy of the complex salt, the center is a quadrivalent carbon cation and the ligands are co-ordinated to the former by lone pair electrons of the latter. One of the lone pair electrons in the ligand is assumed to transfer to the central cation, diminishing the negative charge of the ligand and the positive charge on the central cation. Distribution of such electrons around the central ion should be symmetrical in general and can be represented by linear combinations of the original eigenfunctions of the carbon atom. Then the covalent bonds between the center and the ligands are formed by neutralization of the spin of these electrons. For example, carbon tetrachloride is taken. Four chlorine anions are assumed to co-ordinate around a quadrivalent carbon cation in the following scheme.



If we assume that the eigenfunctions of carbon are similar to those of a hydrogen-like atom and the dependence of the eigenfunctions, $2s$ and $2p$'s on r is nearly the same, the wave-functions of the electrons belonging to the central atom in the state (II) are just as found by Pauling²³ in his ingenious method of hybridization.

$$\left. \begin{aligned} \psi_{\text{III}} &= \frac{1}{2}(s + p_x + p_y + p_z). \\ \psi_{\text{I}\overline{\text{I}}} &= \frac{1}{2}(s + p_x - p_y - p_z). \\ \psi_{\overline{\text{I}}\text{I}} &= \frac{1}{2}(s - p_x - p_y + p_z). \\ \psi_{\overline{\text{I}}\overline{\text{I}}} &= \frac{1}{2}(s - p_x + p_y - p_z). \end{aligned} \right\} \quad \text{(I)}$$

The suffix of ψ is Miller's notation in crystallography, and ψ_{III} , for example, means that the wave-function has its maximal value in the direction of

the normal line to the face (III), one of the tetrahedral faces. In this tetrahedral configuration the resulting molecule is the same as would be derived by the method of Pauling. In short, Pauling started the process from atoms corresponding to the state (II) in the present method. So far as the tetrahedral configuration is concerned, both the methods give the same result and the present method which starts the process from ions seems rather stupid and roundabout compared with the former. This pleonastic process in tetrahedral configuration, however, has been provoked by the requirement of unifying the principle in connection with other configurations, in which the present method has found its true service.

The electrons attached to the central atom in the state (II) neutralize the spin of the electrons of the chlorine atoms as a whole or rather by turns and, therefore, the valence-bond in the state (III) is not formed by a definite pair of electrons, but is of statistical nature. Consequently the number of bonds thus formed has nothing to do with the valency of the atom. The factor which decides the number of bonds is not the valency, but the co-ordination number or the number of ligands in the compound in question. This idea is of especial importance in the trigonal configuration.

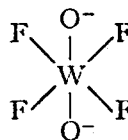
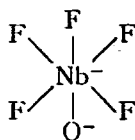
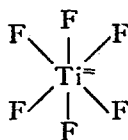
Digonal Configuration.

The molecule of carbon dioxide is considered. It should be noticed here that two similar linear structures are obtained by assuming that the oxygen ion occupies two co-ordinations just as chelate groups, e.g., ethylenediamine, oxalate ion, etc. in complex salts, e. g., $[\text{Co en}_3]\text{Br}_3$, $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$, etc.

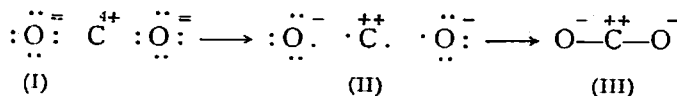
	Central ion	Ligands	Co-ordination number	Resulting molecule
(a)	C^{4+}	$\overset{=}{\text{O}}, \overset{=}{\text{O}}$	2	$\overset{-}{\text{O}} - \overset{++}{\text{C}} - \overset{-}{\text{O}}$ linear
(b)	C^{4+}	$\overset{=}{\text{O}}, \overset{=}{\text{O}}$	4	$\text{O} = \text{C} = \text{O}$ linear

The direction of combination in (a) is one of the Cartesian axes as will be seen below, and that in (b) is also one of the axes, being the bisectrix between the directions of two tetrahedral eigenfunctions in (1). The distance between the carbon and the oxygen atom is not expected to show much difference in the two cases. Thus both the formulæ, $\overset{-}{\text{O}} - \overset{++}{\text{C}} - \overset{-}{\text{O}}$ and $\text{O} = \text{C} = \text{O}$, may be understood as different expressions of similar structures. The difference is provoked by the possibility that the oxygen ion may be assumed to co-ordinate in the alternative ways,

occupying either one or two co-ordinations. The former, however, is preferable to the latter from the following considerations. Complex salts, $K_2[TiF_6]$, $K_2[NbF_6O]$ and $K_2[WF_4O_2]$, are isomorphous. The configuration of these complex ions can be easily derived by the same simple rule of co-ordination as has been applied to simple molecules: viz., the central atom is first ionized and then F^- or O^- is co-ordinated according to the co-ordination number. If the oxygen ion were to occupy two co-ordinations, $[WF_4O_2]^-$ should have a co-ordination number of eight and could not be isomorphous with $[TiF_6]^-$. It can, therefore, be seen that these three complex ions are all octahedral provided that the oxygen ion O^- is equivalent with F^- in co-ordination and occupies only one co-ordination.



Another evidence is furnished by the structure of $PRR'R''O$ ($R=\text{alkyl}$), $H_2PO_2^-$, HPO_4^{2-} and PO_4^{3-} . The tetrahedral configuration of this series also reveals that the oxygen ion occupies one co-ordination. Nielsen and Wand³⁾ have shown by studying Raman spectra that the structure of metaborate ion is $O-B^+-O^-$ instead of $O=B=O$. It is, therefore, postulated in this co-ordination theory that an atom occupies only one co-ordination, the charge of the ligand being independent. In other words, the co-ordination number is not decided by the valency of the atom as ligand, but by the number of atoms which combine directly to the central ion. For example, the co-ordination number of tungsten in $K_2[WF_4O_2]$ is not eight but six, and similarly that of phosphorus in $PRR'R''O$ is four instead of five. Thus O^- as well as F^- occupies one co-ordination and consequently combines to the central ion by a single bond. Now the configuration of carbon dioxide is again considered. Two bivalent oxygen ions are co-ordinated around a quadrivalent carbon cation in the following scheme.



A similar calculation⁴⁾ as in the case of the tetragonal configuration has lead to the following two equivalent wave-functions for the electron distribution around the carbon ion in the state (II).

3) J. R. Nielsen and N. E. Wand, *J. Chem. Phys.*, 5, 201 (1937).

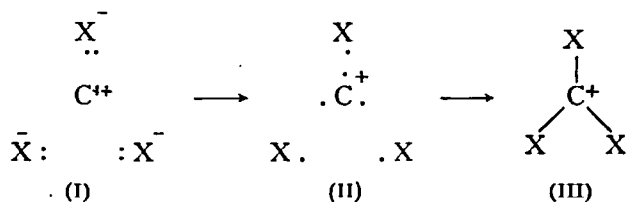
4) The calculation will soon be published in *Rev. Phys. Chem. Japan*.

$$\left. \begin{aligned} \psi_{100} &= \frac{1}{\sqrt{2}}(s+p), \\ \psi_{\bar{1}00} &= \frac{1}{\sqrt{2}}(s-p). \end{aligned} \right\} \quad (2)$$

These functions have their maximum value (1.931) in opposite directions on one of the Cartesian axes.

Trigonal Configuration.

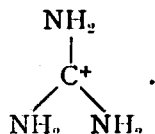
Guanidonium ion is taken for example. Three anions NH_2^- are co-ordinated around a quadrivalent carbon cation in the following scheme, NH_2^- being represented by X^- .



The general rule of symmetrical co-ordination requires that the three ligands are equally co-ordinated around the central ion, and consequently the three electrons attached to the central ion in the state (II) can not belong to any definite one of the original functions, $2s$, $2p_x$, $2p_y$ and $2p_z$. A similar calculation⁵⁾ as above leads to the following three equivalent wave-functions,

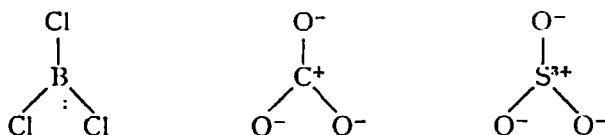
$$\left. \begin{aligned} \psi_{1\bar{1}0} &= \frac{1}{\sqrt{3}}(s+p_x-p_y), \\ \psi_{01\bar{1}} &= \frac{1}{\sqrt{3}}(s+p_y-p_x), \\ \psi_{\bar{1}01} &= \frac{1}{\sqrt{3}}(s+p_z-p_z). \end{aligned} \right\} \quad (3)$$

These functions have their maximum value (1.991) in the directions of bisectrices of two of the Cartesian axes. These three electrons neutralize the spin of those of the amino-groups, and the statistical valence bonds thus produced form a planar trigonal configuration, the angle $\angle \text{XCX}$ being 120° . The results coincide with the X-ray investigation by Theilacker.⁵⁾ The trigonal configuration of the guanidonium ion has thus been explained without assuming the resonance effect, structural formula being simply



5) W. Theilacker, *Z. Krist.*, 76, 203 (1931).

The trigonal structure of other compounds such as BCl_3 , $\text{CO}_3^{=}$, SO_3 , etc. may be derived in similar manners. The structure of the carbonate ion and the molecule of sulphur trioxide are as follows:



Aromatic Bond.

In triphenylmethyl radical, three phenyl ions and an electron are co-ordinated around a central quadrivalent carbon cation. The phenyl ions combine trigonally just as in guanidonium ion by the functions (3), and a steric hindrance of these ions causes an electron to remain in an orbital orthogonal to the former three.

$$\left. \begin{aligned}
 \psi_{1\bar{0}0} &= \frac{1}{\sqrt{3}}(s + p_x - p_y) \\
 \psi_{01\bar{1}} &= \frac{1}{\sqrt{3}}(s + p_y - p_z) \\
 \psi_{\bar{1}01} &= \frac{1}{\sqrt{3}}(s + p_z - p_x) \\
 \psi_{111} &= \frac{1}{\sqrt{3}}(p_x + p_y + p_z)
 \end{aligned} \right\} \quad (4)$$

A transformation of the co-ordinate axes⁹⁾ reveals that the last orbital is identical with one of the original p -orbital, and the direction of its maximum value (1.732) is in the normal line to the trigonal plane of co-ordination.

Benzene molecule can be assumed as having a similar structure. Each carbon atom combines with the adjacent carbon atoms and a hydrogen atom with the three equivalent orbitals in (4) and the fourth electron remains in the fourth orbital. The spin of such electrons of the carbon atoms in benzene ring is opposite alternately and causes an attraction between adjacent aromatic carbon atoms, making the distance (1.42Å) shorter than in paraffins (1.54Å). The fourth electron of the central carbon atom of free triphenylmethyl radical has a spin opposite to those of the aromatic carbon atoms which combine directly to the center, thus giving rise to an anomalous stabilization of the free radical.

Graphite may be explained as an endless net of such aromatic carbon atoms which combine trigonally with the three equivalent orbitals, leaving the electron of the fourth orbital unpaired or rather weakly neutralized by all the three electrons of the adjacent carbon atoms. The distance between the carbon atoms in graphite (1.42Å) is equal to that in benzene, but shorter than that of diamond.

'Double' Bond.

In order to avoid unreasonable different treatments of the 'double' bond and the aromatic link, the same orbitals (4) are assumed to function in both the cases. In ethylene molecule, for example, one carbon atom combines with the other as well as two hydrogen atoms with the three equivalent orbitals, and the fourth electron in the fourth orbital is responsible for the characteristic properties of the unsaturated compound. The angle $\angle \text{HCH}$ of the resulting molecule is 120° for the actual angle⁶⁾ of 118° . The shorter distance (1.32\AA) between the carbon atoms than in the paraffin is due to the attraction exercised by the fourth electrons, and the easy polymerization can also be understood as due to the same origin. The properties of conjugate 'double' bond of butadiene, for example, can also be explained. All the four carbon atoms combine with one another by the trigonal wave-functions (4). The fourth electrons of the inner two carbon atoms partly neutralize their spin on both sides, while those of the outer two can have the opportunity of pairing only on inner side. The outer carbon atoms thus function as the active ends. The anomaly of conjugate 'double' bond in addition reaction can thus be explained. The chemical stability of benzene compared with other 'double' bonds is due to the lack of the active ends.

'Triple' Bond.

A similar consideration as above has lead to a conclusion that the 'triple' bond in acetylene is formed by digonal orbitals (2), superposed by two others. Let the direction of combination of the two carbon atoms be in X-axis, then the wave-functions are as follows.

$$\left. \begin{aligned} \psi_{100} &= \frac{1}{\sqrt{2}}(s + p_z) \\ \psi_{\bar{1}00} &= \frac{2}{\sqrt{2}}(s - p_z) \\ \psi_{010} &= p_y \\ \psi_{001} &= p_z \end{aligned} \right\} \quad (5)$$

The carbon atom combines with the hydrogen and the carbon atom by the digonal functions and the remaining two electrons are weakly paired with those of the other carbon atom. In 'double' bond the fourth electron is in an orbital which is identical with an original p -function and perpendicular to the direction of

6) W. G. Penny, *Proc. Roy. Soc., A*, 158, 306 (1937).

combination of the carbon atoms. Similarly in the 'triple' bond two electrons are in two p -orbitals which are perpendicular to each other and also to the direction of combination. The partial pairing of these electrons gives rise to a stronger attraction than in 'double' bond, the distance between the carbon atoms being very short (1.20\AA).

Summary.

(1) The co-ordination theory of Werner has been extended to simple compounds by regarding all the chemical bonds as co-ordinate links.

(2) The bond is a formal expression of the co-ordinate link. The co-ordination number, therefore, coincides with the number of bonds, whereas the valency has nothing to do with the latter.

(3) The anomalous valence-angle in ammonia and water has been explained by assuming the lone pair of electrons as a sort of ligand. The theoretical bond-angle 109° has been derived, whereas experimental data give 105° and 105° for ammonia and water respectively.

(4) Configuration of various inorganic compounds derived by this method of co-ordination fairly coincides with experimental data.

(5) Configuration of various organic compounds has been dealt with. The bond-functions for these configurations have been given.

(6) The tetrahedral quantization is identical with that of Pauling.

(7) The trigonal quantization has been explained, the eigenfunctions having the strength of 1.991, a little less than 2.000 of the tetrahedral bonds. The planar symmetrical structure of guanidonium cation, carbonate anion, etc. has been explained without assuming the resonance effect.

(8) The digonal quantization gives bonds of a strength of 1.931, weaker than the tetrahedral and trigonal bonds, but far stronger than 1.732 of the original p -functions.

(9) The aromatic quantization has been explained as being composed of the symmetrical trigonal functions and another which is equal to the original p -function in strength and has the maximum value, 1.732 in the direction perpendicular to the trigonal plane.

(10) The structure of free triphenylmethyl radical as well as graphite has been explained.

(11) The 'double' bond is identical with the aromatic bond. Therefore,

the angle \angle HCH in ethylene is 120° theoretically, for 118° from experimental data.

(12) The quantization for the 'triple' bond is composed of the digonal functions and two original p -orbitals, the latter being perpendicular to the former.

*Chemistry Department, Faculty of Science,
Imperial University of Osaka.*

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