Extended Co-ordination Theory. I. Configuration of Simple Compounds of Typical Elements.

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The present paper is to deal with an extension of Werner's co-ordination theory to simple compounds.

Chemical valences are usually classified into electrovalence, covalence and co-ordinate covalence, but it is impossible to draw sharp boundary-lines among them. It is a question of degree than of nature. We can easily understand this fact from the following examples of metallic halides. Whereas stannic chloride forms molecules of the formula $SnCl_4$, chromic chloride is a multinuclear complex(1) in which each chromic ion is surrounded by six chlorine ions octahedrally(2) and each chlorine ion is attached to three chromic ions by co-ordinate covalences. In solid cobaltous chloride, the covalent nature is less remarkable, though its crystal structure(3) shows that it is also a multinuclear complex. Even among bivalent cations we can find covalent compounds such as mercuric chloride which is one of the typical compounds having molecules. The colour of silver bromide is due to the second absorption band,(4) i.e., the co-ordination band, because neither silver nor bromine ion has the first absorption band.(5) The colour of silver iodide is also attributed to the co-ordination band from the same reason, and it is of interest to note that each silver ion is surrounded by four iodine ions tetrahedrally(6) just as in the yellow

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(1) R. Tsuchida, this Bulletin, **13** (1938), 436; *J. Chem. Soc. Japan*, **59** (1938), 586.
(2) N. Wooster, *Z. Krist.*, **74** (1930), 363.
(3) H. Grime and J. A. Santos, *Z. Krist.*, **88** (1934), 136.
(4) R. Tsuchida, this Bulletin, **13** (1938), 388; *J. Chem. Soc. Japan*, **59** (1938), 819.
(5) R. Tsuchida, *J. Chem. Soc. Japan*, **59** (1938), 731.
(6) R. B. Wilsey, *Phil. Mag.*, **46** (1923), 487.

complex ion $[HgI_4]^-$ which has only the second and the third band.(5) In short, solid silver bromide and iodide are not built up purely by electrovalence, but partly by co-ordinate covalence. Sodium chloride is usually regarded as one of the typical ionic compounds, but spectroscopic consideration reveals that it has tendency, though slight, of co-ordination.(1) As can be seen from these examples, it is impossible to distinguish the kinds of valences. For the purpose of the unitary treatment, therefore, every chemical valence may be regarded as a co-ordinate covalence or its extreme case. Thus by assuming that ions and molecules are built up by co-ordinating ions, molecules and electrons around cations, configuration of all the simple as well as complex compounds may be easily found.

The co-ordination is a mutual saturation of co-ordination numbers on both sides of the donor and the acceptor. For example, in $[Cu(NH_3)_4]^{++}$, both the co-ordination numbers of copper and nitrogen are satisfied by co-ordinating NH_3 around Cu^{++}. Any ion in a compound may, therefore, be taken as the center of co-ordination in discussing the configuration of the compound. For the sake of convenience and consistency, however, cations as given by Kossel(7) are chosen as the co-ordination center. Thus in methane quadrivalent carbon cation is taken as the center and four hydrogen anions as ligands. In ammonia three hydrogen anions and a pair of electrons are assumed to co-ordinate around quinquevalent nitrogen cation. The valency of nitrogen, recovering two electrons, is now three. But in ammonium chloride, quinquevalent nitrogen cation is surrounded by four hydrogen anions and the resulting charge of the complex ion is plus one, the valency of nitrogen remaining unchanged.

The typical element, i.e., the element belonging to the subgroup A of the periodic table, is assumed to ionize forming the cation of the charge corresponding to the number of the group. Then the electronic configuration of the cations of the typical elements are as shown in Table 1.

Table 1.

Group	I II III IV V VI VII	Electron distribution of the ion						The lowest co-ordination function
Charge	+ 2+ 3+ 4+ 5+ 6+ 7+	1 s	2 s p	3 s p d	4 s p d f	5 s p d f	6 s p	
Ions	Li Be B C N O F	2						2s
	Na Mg Al Si P S Cl	2	2 6					3s
	K Ca	2	2 6	2 6				4s
	Ga Ge As Se Br	2	2 6	2 6 10				4s
	Rb Sr	2	2 6	2 6 10	2 6			5s
	In Sn Sb Te I	2	2 6	2 6 10	2 6 10			5s
	Cs Ba	2	2 6	2 6 10	2 6 10	2 6		6s
	Tl Pb Bi Po —	2	2 6	2 6 10	2 6 10 14	2 6 10		6s
	— Ra	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	7s

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(7) W. Kossel, *Ann. Physik*, [4], **49** (1916), 229; *Z. Elektrochem.*, **26** (1920), 314.

These cations are co-ordinated with anions and pairs of electrons. Let us now consider the configuration of methane for example. In this compound four hydrogen anions are assumed to co-ordinate around the central quadrivalent carbon cation. All the ligands of a co-ordination compound are co-ordinated so that they may be equally distributed in space. Applying this rule in the present case, the four hydrogen anions should equally divide the space around the central carbon cation. There are two such ways, i.e., the tetragonal and the tetrahedral configuration. Now it is necessary to decide which configuration is more suitable. Let us imagine the electron distribution after co-ordination of the four hydrogen ions, by which four pairs of electrons are introduced. We may expect that these pairs of electrons should be distributed symmetrically by the above mentioned rule and at the same time should satisfy the wave-functions for the carbon ion. Now four functions, 2s, $2p_X$, $2p_Y$ and $2p_Z$, are taken, and then we may expect to find that the symmetry of the resultant electron density distribution is either tetragonal or tetrahedral. The electron density distribution for 2p's together gives an octahedral symmetry, whereas that for 2s a spherical symmetry. The resultant symmetry is, therefore, octahedral. Thus it is easily seen that the tetrahedral configuration completely fits the symmetry. Four hydrogen anions are, therefore, co-ordinated tetrahedrally around the carbon ion, the resulting molecule being similar to that derived by Pauling(8) by the ingenious method of hybridization. In ammonia three hydrogen anions and a pair of electrons are co-ordinated around a quinquevalent nitrogen cation. It is postulated that a pair of electrons has approximately the same share as other anions. Thus the co-ordination number is also four as in methane, and the configuration of ammonia is pyramidal, the angle ∠ HNH being 109°. For water there are two such pairs of electrons, and from a similar reasoning as above, the configuration is V-shaped, the angle ∠HOH being 109°. In all these examples the co-ordination number was four and four eigenfunctions were taken for co-ordination. Let us define such eigenfunctions as co-ordination functions. The lowest co-ordination functions for cations of typical elements are shown in the last column of Table 1. It is postulated that the co-ordination functions could not be of different principal quantum numbers. Then for all the cations of typical elements, the co-ordination function begins with s, because the postulate forbids the participation of 3d functions in co-ordination with 4s and 4p for K^+ and Ca^{++} and so on. Now we can derive the configurations of the compounds of these ions for various co-ordination numbers.

The general rule for co-ordination stated above allows us only six kinds of co-ordination numbers, i.e., 1, 2, 3, 4, 6 and 8. As can be easily seen, the ions of the elements in the first horizontal series in the periodic table, i.e., Li, Be, B, C, N, O and F, could not co-ordinate more than four ligands, because the L-level contains only four eigenfunctions, 2s and $2p^3$, and the above-stated postulate forbids the participation of 3s and 3p in co-ordination with 2s and 2p. The relation between the co-ordination number and the configuration is shown in Table 2 with examples.

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

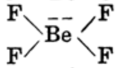
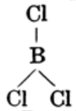
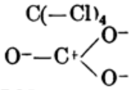
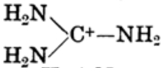
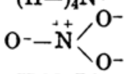
Table 2.

Co-ordination number	Co-ordination functions	Resultant symmetry	Ions and molecules
2	s p	Linear	CO_2, CH_3MgI, BO_2^-, $[FHF]^-$, etc.
3	p p p	Plane-triangular	BCl_3, SO_3, $[C(NH_2)_3]^+$, $CO_3^=$, etc.
4	s p p p	Tetrahedral	CCl_4, $Pb(C_2H_5)_4$, $SO_4^=$, NH_4^+, $[BeF_4]^=$, etc.
6	s p p p d d	Octahedral	SF_6, $[AlF_6]^{3-}$, $[SiF_6]^=$, etc.
8	p p p d d d d d	Hexahedral	$[Ca(C_2H_5OH)_8]^{++}$, etc.

For the co-ordination numbers 3 and 8, the eigenfunction for *s* is not available as is shown in Table 2, because the participation of the function renders it impossible to find the trigonal and the hexahedral symmetry.

Making use of Table 2, we may easily find the configuration of various ions and molecules without any more consideration than the co-ordination number. Examples are given in Table 3 for the elements in the first horizontal series in the periodic table for which the co-ordination numbers, 1, 2, 3 and 4 only are allowed.

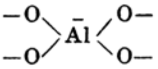
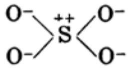
Table 3.

Ion or molecule	Central ion	Ligands	Co-ordination number	Structure	Configuration
$[FHF]^-$	H^+	$2F^-$	2	$F-H^- -F$	Linear
$BeO_2^=$	Be^{++}	$2O^=$	2	$O^- - Be - O^-$	,,
$[BeF_4]^=$	,,	$4F^-$	4		Tetrahedral
BCl_3	B^{3+}	$3Cl^-$	3		Plane-triangular
BO_2^-	,,	$2O^=$	2	$O^- - B^+ - O^-$	Linear
CCl_4	C^{4+}	$4Cl^-$	4	$C(-Cl)_4$	Tetrahedral
$CO_3^=$	,,	$3O^=$	3		Plane-triangular
$[C(NH_2)_3]^+$	,,	$3NH_2^-$	3		Plane-triangular
NH_4^+	N^{5+}	$4H^-$	4	$(H-)_4N^+$	Tetrahedral
NO_3^-	,,	$3O^=$	3		Plane-triangular
$[Li(NH_3)_4]^+$	Li^+	$4NH_3$	4	$(H_3N)_4Li^+$	Tetrahedral

In Table 3 we find $[FHF]^-$, an example of hydrogen bridge. From the present viewpoint, the hydrogen bridge is not so singular as has been usually believed, but one of the special cases of co-ordination. A co-ordination band⁽⁹⁾ due to a hydrogen bridge has been shown in the ultraviolet region. The trigonal configuration of carbonate, nitrate, and guanidonium⁽¹⁰⁾ ions may be easily explained. The complex salts and the simple compounds can be discussed by the same method and their configurations may readily be derived by the same simple consideration. Thus the isomorphism between the sulphates and fluoroborates or orthosilicates and fluoroberyllate may be clearly understood.

The elements of higher atomic number than neon can give ions and molecules of various co-ordination numbers, i.e., 1, 2, 3, 4, 6 and 8. Some of the examples are given in Table 4.

Table 4.

Ion or molecule	Central ion	Ligands	Co-ordination number	Configuration	
CH_3MgI	Mg^{++}	CH_3^-, I^-	2	Linear	
$[AlF_6]^{3-}$	Al^{3+}	$6F^-$	6	Octahedral	
$[AlO_4]^{5-}$	,,	$4O^{=}$	4	Tetrahedral	
$[SiO_4]^{4-}$	Si^{4+}	$4O^{=}$	4	,,	
SO_3	S^{6+}	$3O^{=}$	3	Plane-trigonal	
SF_6	,,	$6F^-$	6	Octahedral	
$SO_4^{=}$	,,	$4O^{=}$	4	Tetrahedral	
PO_4^{3-}	P^{5+}	$4O^{=}$	4	,,	
$H_2PO_2^-$	,,	$2H^-$, $2O^{=}$	4	,,	
ClO_4^-	Cl^{7+}	$4O^{=}$	4	,,	

In Table 4 we find sulphur hexafluoride, a compound of "expanded" shell. The octet theory⁽¹¹⁾ has failed to explain the dodecet structure. The groups SiO_4^{4-} and AlO_4^{5-} are the structural units of various silicate and alumino-silicate minerals.

Anomallies of valence-angles are seen among ions and molecules in which electrons are co-ordinated just as other ligands. For examples in the molecules of ammonia and water, there are pairs of electrons whose spins are neutralized. The present author has devised an automatic method of taking such electrons into consideration, by first removing the electrons from the atom and then co-ordinating them again together with other ligands. This consideration is applicable to all the ions and molecules in which the valencies of the elements of the central cations are lower than the maximum valencies shown by the group numbers in the periodic table. The configuration of such ions and molecules can easily be found automatically without any further consideration by a simple tabular method. Some examples are given in Table 5. In the first column

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(9) R. Tsuchida and T. Tsumaki, this Bulletin, **13** (1938), 527.
(10) W. Theilacker, *Z. Krist.*, **76** (1931), 203.
(11) I. Langmuir, *J. Am. Chem. Soc.*, **41** (1919), 252.

is written the ion or molecule whose configuration is required. Then the ligands are tabulated, a pair of electrons and an odd electron being treated just as other ligands. The number of electrons to be co-ordinated can be readily found by balancing the valency of the central ion and the charges of the ligands with that of the entire ion or molecule. Then the co-ordination number is found, which in turn gives the configuration by Table 2.

Table 5.

Ion or molecule	Central ion	Ligands	Co-ordination number	Configuration	Angle		
					Theoretical	Observed	Literature
H_2O	O^{6+}	$2H^-$, :, :	4	V-shaped	109°	105°	
NH_3	N^{5+}	$3H^-$, :	4	Pyramidal	109°	106°	
NO_2^-	,,	$2O^{=}$, :	3	V-shaped	120°	132°	(12)
NO_2	,,	$2O^{=}$, ·	3	,,	120°	110°–120°	(13)
CO_2	C^{4+}	$2O^{=}$	2	Linear	180°	180°	
SO_2	S^{6+}	$2O^{=}$, :	3	V-shaped	120°	122°	(14)
SO_3	,,	$3O^{=}$	3	Trigonal	120°	120°	(15)
$SO_3^{=}$	,,	$3O^{=}$, :	4	Pyramidal	109°	111°	(16)
ClO_2^-	Cl^{7+}	$2O^{=}$, :, :	4	V-shaped	109°	114°	(17)
ClO_3^-	,,	$3O^{=}$, :	4	Pyramidal	109°	107°	(18)

The angles derived by this method fairly coincide with the experimental data as can be seen from the table.

As is evident from Tables 2–5, the configuration of a molecule or an ion is determined only by the co-ordination number, if appropriate consideration is given to "non-bonding" electrons.

Summary.

All the chemical linkages may be explained in terms of the co-ordinate covalence. By assuming that molecules and radical ions are built up by co-ordination of molecules, ions and electrons as ligands around central cations whose combining fields are given by sets of wave-functions, the configuration of all the simple as well as complex compounds could be readily found.

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(12) W. H. Zachariasen, *J. Am. Chem. Soc.*, **53** (1931), 2123.
(13) G. Sutherland and W. G. Penny, *Nature*, **136** (1935), 146.
(14) P. C. Cross and L. D. Brockway, *J. Chem. Phys.*, **3** (1935), 821.
(15) H. Gerding and J. Lecomte, *Nature*, **142** (1938), 718.
(16) W. H. Zachariasen and N. E. Buckley, *Phys. Rev.*, **37** (1931), 1295.
(17) G. R. Levi and A. Scherillo, *Z. Krist.*, **76** (1930), 431.
(18) W. H. Zachariasen, *Z. Krist.*, **71** (1929), 517.