

EXTENDED CO-ORDINATION THEORY OF VALENCY. IV.

Configuration of Compounds of Transition Elements.

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It has already been perceived by Werner that the concept of complex formation is an important generalization throughout inorganic chemistry. The attempt of the work reported in this series of papers is to extend his co-ordination theory to wider scope, not only to inorganic simple compounds but also to organic ions and molecules. In the preceding papers¹⁾²⁾³⁾ it has been shown that the configuration of compounds of typical elements can be found merely by regarding all the chemical linkages as co-ordinate covalences and applying the rule of symmetrical co-ordination: in other words, the configuration of molecules and ions is given by simply co-ordinating around a central cation a few ions, polar molecules and, in special cases, electrons. The present paper deals with the configuration of compounds of transition elements. It is, however, convenient to summarize briefly the treatment of typical elements before taking up compounds of transition elements, since the latter can be treated in a similar manner to the former.

Configuration of Compounds of Typical Elements.

The method of finding configuration of compounds of typical elements is as follows.

- (1) The central ion or atom is deprived of its electrons till there results a cation whose effective atomic number is equal to the atomic number of the nearest inert-gas element or the last member of the eighth group of the periodic table, i. e., nickel, palladium or platinum.
- (2) Around the cation are co-ordinated ions, molecules and electrons.
- (3) The number of electrons to be co-ordinated is found by the formula,

$$n = C - \sum L - K,$$

1) R. Tsuchida, *Bull. Chem. Soc. Japan*, **14**, 101 (1939).

2) R. Tsuchida, *This Journal*, **13**, 31 (1939).

3) R. Tsuchida and M. Kobayashi, *This Journal*, **13**, 61 (1939).

where C , L and K are respectively the charges of the central cation, the ligand anion and the radical ion whose configuration is required, and n is the number of electrons to be co-ordinated.

(4) The pairs of such electrons are treated just as other ligands in co-ordination, though they are latent in the external configuration. Accordingly the term 'co-ordination number' is here used in a wider sense, meaning the total number of ligands including the pairs of electrons besides ions and molecules.

(5) The co-ordination number, together with the rule of symmetrical co-ordination, decides the quantization around the central ion. According as the co-ordination number is two, three, four, six or eight, the quantization is digonal, trigonal, tetrahedral, octahedral or cubic. The quantizations are given below.

(6) If the ion or molecule whose configuration is required contains as ligands only ions and molecules but no electrons, the configuration has the same symmetry as the quantization. If, on the contrary, the ion or molecule in question has besides these ligands a pair or pairs of electrons as imaginary ligands, the configuration is different from that expected from the number of the apparent ligands. For instance, SO_2 , NO_2^- , etc. have as latent ligand one pair of electrons each, and therefore the co-ordination number is three. Other triatomic ions and molecules such as ClO_2^- , H_2O , etc. have two pairs of electrons, and hence the co-ordination number is four. In spite of the difference in the co-ordination number, however, the external configuration is V-shaped all alike. Contribution of these electrons can be perceived only in the difference of the bending angle which is 120° for the former group and 109° for the latter. It is also due to such electrons that the form of NH_3 , SO_4^{2-} , etc. is pyramidal instead of being a plane triangle.

Some examples of finding the configuration are shown in Table I.

Table I.

| Ion or molecule | Central cation | Apparent ligands | C | ΣL | K | n | Electron pairs | Co-ordination number | Quantization | Configuration |
|---------------------|------------------|------------------|-----|------------|-----|-----|----------------|----------------------|--------------|-----------------------------|
| BeO_2^{2-} | Be^{++} | 2 O^- | 2 | 4 | -2 | 0 | 0 | 2 | digonal | linear (180°) |
| CO_2 | C^{++} | 2 O^- | 4 | 4 | 0 | 0 | 0 | 2 | " | " |
| NO_2^- | N^{5+} | 2 O^- | 5 | 4 | -1 | 2 | 1 | 3 | trigonal | V-shaped (120°) |
| SO_2 | S^{6+} | 2 O^- | 6 | 4 | 0 | 2 | 1 | 3 | " | " |
| ClO_2^- | Cl^{7+} | 2 O^- | 7 | 4 | -1 | 4 | 2 | 4 | tetrahedral | V-shaped (109°) |
| OH_2 | O^{6+} | 2 H^- | 6 | 2 | 0 | 4 | 2 | 4 | " | " |
| SO | S^{6+} | O^- | 6 | 2 | 0 | 4 | 2 | 3 | trigonal | |
| SO_2 | " | 2 O^- | " | 4 | 0 | 2 | 1 | 3 | " | triangular (120°) |
| SO_3 | " | 3 O^- | " | 6 | 0 | 0 | 0 | 3 | " | " |
| SO_3^{2-} | " | 3 O^- | " | 6 | -2 | 2 | 1 | 4 | tetrahedral | pyramidal (109°) |
| SO_4^{2-} | " | 4 O^- | " | 8 | -2 | 0 | 0 | 4 | " | tetrahedral (109°) |
| SF_6 | " | 6 F^- | " | 6 | 0 | 0 | 0 | 6 | octahedral | octahedral (90°) |

Quantization around the Central Ion.

The co-ordination takes place by setting lone-pair electrons of ligands in the orbitals around the central ion, according to the rule of symmetrical co-ordination and at the same time satisfying certain wave-mechanical conditions. Such orbitals must be equally and symmetrically distributed around the central ion, and the ways of dividing the space around a center into equal parts symmetrically are naturally limited in number, that is, to divide into two, three, four, six, eight, etc. Accordingly the quantization around the central ion must consist of as many eigenfunctions, and is digonal, trigonal, tetrahedral, tetragonal, octahedral or cubic.

The zeroth order eigenfunctions for the tetrahedral bonds in carbon compounds have been derived by Pauling⁴⁾ and the quantization, just as it is, can be applied to other co-ordination compounds. By a similar calculation, the present authors³⁾ have obtained the digonal and the trigonal quantization.

The digonal quantization.

$$\begin{cases} \psi_{100} = \frac{1}{\sqrt{2}}(s + p_x). \\ \psi_{\bar{1}00} = \frac{1}{\sqrt{2}}(s - p_x). \end{cases} \quad (1)$$

The trigonal quantization.

$$\begin{cases} \psi_{1\bar{1}0} = \frac{1}{\sqrt{3}}(s + p_x - p_y). \\ \psi_{01\bar{1}} = \frac{1}{\sqrt{3}}(s + p_y - p_z). \\ \psi_{\bar{1}01} = \frac{1}{\sqrt{3}}(s + p_z - p_x). \end{cases} \quad (2)$$

The tetrahedral quantization.

$$\begin{cases} \psi_{111} = \frac{1}{2}(s + p_x + p_y + p_z). \\ \psi_{\bar{1}\bar{1}\bar{1}} = \frac{1}{2}(s + p_x - p_y - p_z). \\ \psi_{\bar{1}1\bar{1}} = \frac{1}{2}(s - p_x + p_y - p_z). \\ \psi_{1\bar{1}1} = \frac{1}{2}(s - p_x - p_y + p_z). \end{cases} \quad (3)$$

Whereas for elements whose atomic number is less than ten are not allowed co-ordination numbers higher than four,¹⁾ there are, however, sexa-coördinate and

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

octa-coördinate compounds for elements of higher atomic numbers. The following octahedral functions derived by the present authors⁵⁾ are somewhat different from those by Pauling.⁴⁾

The octahedral quantization.

$$\left\{ \begin{array}{l} \psi_{001} = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{2}}p_z + \frac{1}{\sqrt{3}}d_z \\ \psi_{00\bar{1}} = \frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{2}}p_z + \frac{1}{\sqrt{3}}d_z \\ \psi_{100} = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{2}}p_x - \frac{1}{\sqrt{12}}d_z + \frac{1}{2}d_x \\ \psi_{\bar{1}00} = \frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{2}}p_x - \frac{1}{\sqrt{12}}d_z + \frac{1}{2}d_x \\ \psi_{010} = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{2}}p_y - \frac{1}{\sqrt{12}}d_z - \frac{1}{2}d_x \\ \psi_{0\bar{1}0} = \frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{2}}p_y - \frac{1}{\sqrt{12}}d_z - \frac{1}{2}d_x \end{array} \right. \quad (4)$$

The plane tetragonal configuration, as is found in bivalent platinous compounds, belongs to the octahedral quantization, and will be discussed below. The cubic quantization derived by the present authors⁵⁾ is as follows.

The cubic quantization.

$$\left\{ \begin{array}{l} \psi_{111} = \frac{1}{\sqrt{8}}(s + p_x + p_y + p_z + d_{xy} + d_{yz} + d_{zx}) + \frac{\sqrt{3}}{4\sqrt{2}}d_x + \frac{1}{4\sqrt{2}}d_z \\ \psi_{11\bar{1}} = \frac{1}{\sqrt{8}}(s + p_x + p_y - p_z + d_{xy} - d_{yz} - d_{zx}) - \frac{\sqrt{3}}{4\sqrt{2}}d_x - \frac{1}{4\sqrt{2}}d_z \\ \psi_{1\bar{1}1} = \frac{1}{\sqrt{8}}(s + p_x - p_y + p_z - d_{xy} - d_{yz} + d_{zx}) - \frac{\sqrt{3}}{4\sqrt{2}}d_x - \frac{1}{4\sqrt{2}}d_z \\ \psi_{\bar{1}11} = \frac{1}{\sqrt{8}}(s - p_x + p_y + p_z - d_{xy} + d_{yz} - d_{zx}) - \frac{\sqrt{3}}{4\sqrt{2}}d_x - \frac{1}{4\sqrt{2}}d_z \\ \psi_{1\bar{1}\bar{1}} = \frac{1}{\sqrt{8}}(s + p_x - p_y - p_z - d_{xy} + d_{yz} - d_{zx}) + \frac{\sqrt{3}}{4\sqrt{2}}d_x + \frac{1}{4\sqrt{2}}d_z \\ \psi_{\bar{1}1\bar{1}} = \frac{1}{\sqrt{8}}(s - p_x + p_y - p_z - d_{xy} - d_{yz} + d_{zx}) + \frac{\sqrt{3}}{4\sqrt{2}}d_x + \frac{1}{4\sqrt{2}}d_z \\ \psi_{\bar{1}\bar{1}1} = \frac{1}{\sqrt{8}}(s - p_x - p_y + p_z + d_{xy} - d_{yz} - d_{zx}) + \frac{\sqrt{3}}{4\sqrt{2}}d_x + \frac{1}{4\sqrt{2}}d_z \\ \psi_{\bar{1}\bar{1}\bar{1}} = \frac{1}{\sqrt{8}}(s - p_x - p_y - p_z + d_{xy} + d_{yz} + d_{zx}) - \frac{\sqrt{3}}{4\sqrt{2}}d_x - \frac{1}{4\sqrt{2}}d_z \end{array} \right. \quad (5)$$

5) R. Tsuchida and M. Kobayashi, not yet published.

The suffixes (110), (111), etc. show that the functions have maxima in the directions of the normal lines to the faces (110), (111), etc. in Miller's notation.

In some special cases are required nine eigenfunctions. As an example may be cited $K_4[W(CN)_6]$, of which the electronic distribution will be discussed later. The set of nine eigenfunctions consists of the cubic functions (5) and the ninth, ψ_{xyz} (6), which is normalized in itself and orthogonal to the cubic functions. A similar case is found in the aromatic quantization.²³⁾

$$\psi_{xyz} = \frac{1}{2} d_x - \frac{\sqrt{3}}{2} d_z \tag{6}$$

The original eigenfunctions are as follows.

$$\left\{ \begin{array}{l} s = 1, \\ p_x = \sqrt{3} \sin \theta \cos \varphi, \\ p_y = \sqrt{3} \sin \theta \sin \varphi, \\ p_z = \sqrt{3} \cos \theta. \end{array} \right. \left\{ \begin{array}{l} d_{xy} = \frac{\sqrt{15}}{2} \sin^2 \theta \sin 2\varphi, \\ d_{yz} = \sqrt{15} \sin \theta \cos \theta \sin \varphi, \\ d_{zx} = \sqrt{15} \sin \theta \cos \theta \cos \varphi, \\ d_x = \frac{\sqrt{15}}{2} \sin^2 \theta \cos 2\varphi, \\ d_z = \frac{\sqrt{5}}{2} (3 \cos^2 \theta - 1). \end{array} \right. \tag{7}$$

The bond strength of these quantizations as well as that for the original functions is shown in Table II.

Table II.

| Eigenfunction | | Maximum value in ϕ_{kk} |
|---------------|--|------------------------------|
| Original | s | 1.000 |
| | f_x, f_y, f_z | 1.732 |
| | $d_{xy}, d_{yz}, d_{zx}, d_x$ | 1.936 |
| | d_z | 2.236 |
| Digonal | $\psi_{100}, \psi_{\bar{1}00}$ | 1.931 |
| Trigonal | $\psi_{1\bar{1}0}, \psi_{01\bar{1}}, \psi_{\bar{1}0\bar{1}}$ | 1.991 |
| Tetrahedral | $\psi_{111}, \psi_{1\bar{1}\bar{1}}, \psi_{\bar{1}1\bar{1}}, \psi_{\bar{1}\bar{1}1}$ | 2.000 |
| Octahedral | $\psi_{100}, \psi_{\bar{1}00}, \psi_{010}, \psi_{0\bar{1}0}, \psi_{001}, \psi_{00\bar{1}}$ | 2.924 |
| Cubic | $\psi_{111}, \psi_{1\bar{1}\bar{1}}, \psi_{\bar{1}1\bar{1}}, \psi_{\bar{1}\bar{1}1}, \psi_{1\bar{1}1}, \psi_{\bar{1}11}, \psi_{11\bar{1}}, \psi_{\bar{1}\bar{1}\bar{1}}$ | 2.816 |
| Aromatic | $\phi_{111} = \frac{1}{\sqrt{3}} (f_x + f_y + f_z)$ | 1.732 |
| Ninth | $\psi_{xyz} = \frac{1}{2} d_x - \frac{\sqrt{3}}{2} d_z$ | 2.236 |

As can be seen from Table II, the octahedral quantization gives the strongest bond (2.924). It may be understood as the reason why the octahedral configura-

tion so predominates throughout the elements, except the ten lightest elements for which, as has been mentioned above, the quantization more complicated than the tetrahedral is impossible. Also the fact that the configuration of quadri-coordinate complexes of transition elements which have several electrons in incomplete *d*-shell is coplanar instead of being tetrahedral may be explained as due to this extraordinary bond strength of the octahedral quantization. As regards this problem, it will be treated later.

Classification of Compounds of Transition Elements.

Ions and molecules containing transition elements can be classified into five groups according to the effective atomic number of their central ions or atoms. The first group includes the compounds whose central ions are of the inert-gas type, or in other words, have the effective atomic number equal to that of an inert-gas element. Such compounds may be represented by chromate, permanganate, zirconate, hexachlorozirconate, etc. which correspond to sulphate, perchlorate, orthosilicate, fluorosilicate, etc. The second group consists of the compounds whose central ion has the same effective atomic number as trivalent luthenic ion, i.e., 68. This group is exemplified by perrhenate ion which correspond to perchlorate ion among the compounds of typical elements and also to permanganate ion in the first group. To the third group belong the compounds which have central ions or atoms of the same effective atomic number as nickel, palladium or platinum. As examples of such compounds may be cited nickel carbonyl, mercuric chloride, and many colourless complexes, e.g., $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{Cu}(\text{CN})_4]^{2-}$, $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$, etc. A number of compounds of typical elements such as $[\text{SnCl}_6]^{2-}$, $\text{Pb}(\text{C}_2\text{H}_3)_4$, etc. belong to the same type as this group. The fourth group includes all the rare-earth compounds except those belonging to the first and the second group. In these compounds, however, the unsaturated *4f*-shell is screened by *5s*- and *5p*-shells, and, therefore, the behaviour of the central ion in chemical combination is similar to those of the first group. The fifth and the last group contains the compounds whose central ions are unsaturated in *d*-shells. Since only this group is subjected to different treatment from others in finding the configuration, it is more convenient to classify the compounds of transition elements into two kinds. The compounds of the first, the second, the third and the fourth group belong to the first kind, and those of the fifth with unsaturated *d*-shells to the second.

Examples of these groups are given in Table III.

Table III.

| Kind | Group | Example | Central ion | Effective atomic no. | Electronic configuration. | | | | | | | | | | | | | |
|-------------------------|--|--|------------------|-----------------------|---------------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | 1s | 2s | 2p | 3s | 3p | 3d | 4s | 4p | 4d | 4f | 5s | 5p | 5d | |
| 1 | 1 Inert-gas type | CrO ₄ ²⁻ | Cr ⁶⁺ | 18(A) | 2 | 2 | 6 | 2 | 6 | | | | | | | | | |
| | | [ZrCl ₆] ²⁻ | Zr ⁴⁺ | 36(Kr) | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | | | | | | |
| | | [La(NH ₃) ₈] ³⁺ | La ³⁺ | 54(Xe) | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | | | 2 | 6 | |
| | 2 Pseudo-inert-gas type | ReO ₄ ⁻ | Re ⁷⁺ | 68(La ³⁺) | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | 14 | | | 2 | 6 |
| 3 Noble-metal type | [Ag(NH ₃) ₂] ⁺ | Ag ⁺ | 46(Pd) | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | | | | | | |
| | HgCl ₂ | Hg ²⁺ | 78(Pt) | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | 14 | | | 2 | 6 | 10 |
| 4 Rare-earth complex | [Yl(NH ₃) ₈] ³⁺ | Yl ³⁺ | 67 | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | 14 | | | 2 | 6 | |
| 2 | 5 Unsaturated transition type | [Fe(CN) ₆] ³⁻ | Fe ³⁺ | 23 | 2 | 2 | 6 | 2 | 6 | 5 | | | | | | | | |
| | | [PtCl ₆] ²⁻ | Pt ⁴⁺ | 74 | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | 14 | | | 2 | 6 |

Configuration of Compounds of the First Kind of Transition Elements.

By a method quite similar to that for typical elements, the configuration of compounds of transition elements of this kind can be found very simply, even more simply than in the cases for the former. The configuration is digonal, trigonal, tetrahedral, octahedral or cubic according as the co-ordination number is two, three, four, six or eight respectively. Examples are shown in Table IV.

Table IV.

| Group | Ion or molecule | Central ion | Effective atom. no. | Ligands | Co-ord. number | Quantization and configuration |
|-------|--|------------------|-----------------------|-------------------------------------|----------------|--------------------------------|
| 1 | CrO ₄ ²⁻ | Cr ⁶⁺ | 18(A) | 4O ²⁻ | 4 | tetrahedral |
| | CrO ₂ Cl ₂ | " | " | 2O ²⁻ ; 2Cl ⁻ | " | " |
| | ZrO ₄ ⁴⁻ | Zr ⁴⁺ | 36(Kr) | 4O ²⁻ | " | " |
| | [ZrCl ₆] ²⁻ | " | " | 6Cl ⁻ | 6 | octahedral |
| | [MoO ₃ F ₃] ²⁻ | Mo ⁶⁺ | " | 3O ²⁻ ; 3F ⁻ | " | " |
| | [CeCl ₆] ²⁻ | Ce ⁴⁺ | 54(Xe) | 6Cl ⁻ | " | " |
| 2 | [La(NH ₃) ₈] ³⁺ | La ³⁺ | " | 8NH ₃ | 8 | cubic |
| | ReO ₄ ⁻ | Re ⁷⁺ | 68(La ³⁺) | 4O ²⁻ | 4 | tetrahedral |
| | [WO ₂ F ₄] ⁻ | W ⁶⁺ | " | 2O ²⁻ ; 4F ⁻ | 6 | octahedral |
| | OsF ₈ | Os ⁸⁺ | " | 8F ⁻ | 8 | cubic |

| | | | | | | |
|---|--|------------------|--------|--------------------------|---|-------------|
| 3 | $\text{Ni}(\text{CO})_4$ | Ni | 28(Ni) | 4CO | 4 | tetrahedral |
| | $[\text{CuCl}_3]^-$ | Cu^+ | " | 3 Cl^- | 3 | trigonal |
| | $\text{Zn}(\text{C}_2\text{H}_5)_2$ | Zn^{2+} | " | 2 C_2H_5 | 2 | digonal |
| | $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ | " | " | 6 H_2O | 6 | octahedral |
| | $[\text{Ag}(\text{NH}_3)_2]^+$ | Ag^+ | 46(Pd) | 2 NH_3 | 2 | digonal |
| | $[\text{Cd}(\text{NH}_3)_4]^{2+}$ | Cd^{2+} | " | 4 NH_3 | 4 | tetrahedral |
| | HgCl_2 | Hg^{2+} | 78(Pt) | 2 Cl^- | 2 | digonal |
| 4 | $[\text{Pr}(\text{NH}_3)_8]$ | Pr^{3+} | 56 | 8 NH_3 | 8 | cubic |

Configuration of Compounds of the Second Kind of Transition Elements.

Whereas the central ion of compounds except those of the fifth group contains no or ten *d*-electrons, in compounds of the fifth group, however, the *d*-shell of the central ion is neither empty nor full. These *d*-electrons, their energy levels being nearly equal to the co-ordination level, seem to have more or less influence on the co-ordination quantization. When there are six ligands, however, the configuration is octahedral, no matter how the *d*-shell may be. This fact may be understood by assuming that the octahedral bond is so strong that the configuration is scarcely affected by the existence of unsaturated *d*-shell.

The configuration of quadri-coördinate compounds of the second kind is planar instead of being tetrahedral. For example the effective atomic number of cupric ion in $[\text{Cu}(\text{NH}_3)_4]^{++}$ is 27, i.e., there are nine *d*-electrons. The configuration of such compounds can be easily understood by assuming that the octahedral quantization is the most stable and many central ions have strong tendency to take this quantization if the condition is favourable. In $[\text{Cu}(\text{NH}_3)_4]^{++}$ there are only four ligands and two pairs of electrons are required to complete the octahedral quantization. It is assumed that these electrons are supplied from the incomplete *d*-shell. Then four electrons in two pairs are co-ordinated around the cupric ion with four ammonia molecules. Here again the rule of symmetrical co-ordination requires that the four ammonia molecules are arranged in a plane and the two pairs of electrons in the two orbitals perpendicular to the plane. The apparent configuration, therefore, is square, the electrons being latent in the external configuration.

The participation of two pairs of electrons in formation of the quadri-coördinate complexes is analogous to the co-ordination of pairs of electrons in simple molecules and radical ions of typical elements, such as NH_3 , H_2O , SO_3^- , etc.

It is interesting to note that there has never been found a planar complex whose central ion has three or less *d*-electrons. This fact supports the hypothesis

that the square configuration results from the octahedral quantization by the participation of two pairs of d -electrons.

Similar cases are found when eight ligands are co-ordinated around an ion of a transition element which has an unsaturated d -shell. For example the central ion of $[\text{W}(\text{CN})_8]^{4-}$ has 70 electrons, of which 68 fill orbits completely up to $5p$ and two belong to $5d$ -shell. Such a pair of electrons participates in co-ordination with eight cyanide ions to saturate the nine co-ordination orbitals, i.e., the cubic functions (5) and the ninth (6). Also in this case requires the rule of symmetrical co-ordination the electron pair to be in the ninth orbital.

Examples of finding the configuration of complex ions of the unsaturated transition type are given in Table V.

Table V.

| Complex ion | Centr. ion | Effect. at. no. | d -Electrons | | Ligands | Co-ord. number | Quantization | Configuration |
|--|------------------|-----------------|----------------|--------------|-------------------------------------|----------------|-----------------|---------------|
| | | | In d -shell | co-ordinated | | | | |
| $[\text{Fe}(\text{CN})_6]^{4-}$ | Fe^{2+} | 24 | 6 | 0 | 6CN^- | 6 | octahedral | octahedral |
| $[\text{Co}(\text{NH}_3)_6]^{3+}$ | Co^{3+} | 24 | 6 | 0 | 6NH_3 | 6 | " | " |
| $[\text{Cr}(\text{NH}_3)_6]^{3+}$ | Cr^{3+} | 21 | 3 | 0 | 6NH_3 | 6 | " | " |
| $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ | Cu^{2+} | 27 | 5 | 4 | $4\text{H}_2\text{O}; 2:$ | 6 | " | square |
| $[\text{Ag}(\text{C}_5\text{H}_5\text{N})_4]^{2+}$ | Ag^{2+} | 45 | 5 | 4 | $4\text{C}_5\text{H}_5\text{N}; 2:$ | 6 | " | " |
| $[\text{PtCl}_4]^{2-}$ | Pt^{2+} | 76 | 4 | 4 | $4\text{Cl}^-; 2:$ | 6 | " | " |
| $[\text{PtCl}_6]^{4-}$ | Pt^{4+} | 74 | 6 | 0 | 6Cl^- | 6 | " | octahedral |
| $[\text{W}(\text{CN})_8]^{4-}$ | W^{3+} | 70 | 0 | 2 | $8\text{CN}^-; 2:$ | 9 | nine-functioned | cubic |

: a pair of electrons

Configuration of Sexa-coördinate Complex Ions.

It is now possible to predict the configuration, if only the composition of an ion or a molecule is given. A number of examples have already been shown above and in the preceding papers, but it is not unnecessary to add some more examples together with the empirical data for quadri-coördinate and sexa-coördinate complexes of transition elements.

It has been stated that the configuration of sexa-coördinate compounds of transition elements as well as of typical elements is octahedral. Ions and molecules whose configuration has been proved as octahedral are shown in Table VI.

It is of interest to note that complexes of central ions whose effective atomic number is 21, 24, 42 or 74 surpass in number those of the effective atomic number of the corresponding inert-gas or pseudo-inert-gas element. This fact is due to the stability of complexes of trivalent chromium, bivalent iron, trivalent

Table VI.

| Effective at. no. of the centr. ion | Complex ions |
|--|---|
| 18 | [TiCl ₆] ²⁻ , etc. |
| 21 | [Cr(H ₂ O) ₆] ³⁺ , [CrF ₅ H ₂ O] ⁼ , [Cr(NH ₃) ₅ Cl] ²⁺ , [Cr(NH ₃) ₆] ³⁺ , [Cr(NH ₃) ₅ H ₂ O] ³⁺ , etc. |
| 23 | [Mn(NH ₃) ₆] ²⁺ , [FeF ₆] ³⁻ , etc. |
| 24 | [Fe(NH ₃) ₆] ²⁺ , [Fe(NO ₂) ₆] ⁴⁻ , [Co(NO ₂) ₆] ³⁻ , [Co(NH ₃) ₆] ³⁺ , [Co(NH ₃) ₅ Cl] ²⁺ , [Co(NH ₃) ₅ H ₂ O] ³⁺ , [Co(NH ₃) ₅ (NO ₂) ₄] ⁻ , [Co(NH ₃) ₆] ²⁺ , etc. |
| 25 | [Co(NH ₃) ₆] ²⁺ , etc. |
| 26 | [Ni(NH ₃) ₆] ²⁺ , [Ni(CH ₃ NH ₂) ₆] ²⁺ , [Ni(NO ₂) ₆] ⁴⁻ , etc. |
| 27 | [CuCl ₄ (H ₂ O) ₂] ⁼ , etc. |
| 28 | [Zn(H ₂ O) ₆] ²⁺ , [Zn(NH ₃) ₆] ²⁺ , etc. |
| 36 | [ZrCl ₆] ⁼ , [MoO ₃ F ₃] ³⁻ , [ZrF ₆] ⁼ , etc. |
| 42 | [Rh(NO ₂) ₆] ³⁻ , [Rh(NH ₃) ₅ Cl] ²⁺ , etc. |
| 46 | [Cd(NH ₃) ₆] ²⁺ , etc. |
| 70 | [OsO ₂ Cl ₄] ⁼ , etc. |
| 72 | [OsCl ₆] ⁼ , [OsBr ₆] ⁼ , etc. |
| 74 | [Ir(NO ₂) ₆] ³⁻ , [PtCl ₆] ⁼ , [PtBr ₆] ⁼ , [Pt(SCN) ₆] ⁼ , etc. |

cobalt, trivalent rhodium, trivalent iridium and quadrivalent platinum. The stability of these complexes in turn suggests the stable electronic configuration in the *d*-shell, which is clear from the following table.

Table VII.

| Effect. at. no. | Stable complex | Electronic configuration | |
|--------------------|--|--------------------------|-----------------|
| | | Inert-gas kernel | <i>d</i> -Shell |
| 21 | [Cr(NH ₃) ₆] ³⁺ | 18 (A) | 3 |
| 24 | [Fe(CN) ₆] ⁴⁻ | 18 " | 6 |
| | [Co(NH ₃) ₆] ³⁺ | 18 " | 6 |
| 42 | [Rh(NH ₃) ₅ Cl] ²⁺ | 36 (Kr) | 6 |
| 74 | [Ir(NO ₂) ₆] ³⁻ | 68 (Lu ³⁺) | 6 |
| | [PtCl ₆] ⁼ | 68 " | 6 |

It is, therefore, assumed that the electronic configuration in the *d*-shell of a complex has a similar symmetry to its external configuration. In order that the three or six electrons have an octahedral symmetry, they must occupy a Stoner grouplet, i.e., a set of orbitals represented by d_{xy} , d_{yz} and d_{zx} .

Configuration of Quadri-coördinate Complex Ions.

It can be predicted that the configuration of quadri-coördinate ions and molecules is tetrahedral, except those whose central ions have four to nine *d*-electrons, and the configuration of the latter is square. Quadri-coördinate com-

pounds of transition elements whose configuration is known as tetrahedral are tabulated below.

Table VIII.

| Effective at. no. of the centr. ion | Ions and molecules |
|-------------------------------------|--|
| 18 ⁻ | VO ₄ ³⁻ , VS ₄ ³⁻ , CrO ₄ ⁼ , MnO ₄ ⁻ , etc. |
| 28 | Ni(CO) ₄ , [Cu(CN) ₄] ³⁻ , [Cu(S=C < NH ₂) ₄] ⁺ , [Zn(CN) ₄] ⁼ , ZnO ₄ ²⁻ , etc. |
| 36 | MoO ₄ ⁼ , etc. |
| 46 | [Ag(β-oxychinolin) ₂] ⁺ , [Cd(CN) ₄] ⁼ , etc. |
| 68 | WO ₄ ⁼ , ReO ₄ ⁻ , etc. |
| 74 | [Pt(CH ₃) ₃ Cl]. |
| 78 | [Hg(CN) ₄] ⁼ , etc. |

A platinum complex [Pt(CH₃)₃Cl] has six *d*-electrons and the configuration is expected to be planar, but nevertheless it is tetrahedral according to Cox and Webster.⁶⁾ This is the only contradiction so far encountered.

Quadri-coördinated ions and molecules which have been proved to be planar are given in Table IX.

Table IX.

| Effective at. no. of the centr. ion | Ions and molecules |
|-------------------------------------|--|
| 25 | [CoCl ₂ (C ₅ H ₅ N) ₂]. |
| 26 | [Ni(CN) ₄] ⁼ , [Ni(S ₂ C ₂ O ₂) ₂] ⁼ , [Ni(salicylaldoxim) ₂], [NiX ₂ (R ₃ P) ₂], [Ni ₂ (Δs(C ₂ H ₅) ₂) ₂], etc. |
| 27 | [Cu(H ₂ O) ₄] ⁺⁺ , [Cu(salicylaldoxim) ₂], [Cu(acetylaceton) ₂], [Cu(benzylacetone) ₂], [Cu(dipropionylmethane) ₂], [Cu(3-chloroacetylaceton) ₂], [CuCl ₂ (C ₅ H ₅ N) ₂], [CuCl ₂ dimethylglyoxim], [Cu(picolinic acid) ₂], etc. |
| 44 | [Pd(CN) ₄] ⁼ , [PdCl ₄] ⁼ , [Pd(NH ₃) ₄] ⁺⁺ , [Pd en ₂] ⁺⁺ , [Pd(S ₂ C ₂ O ₂) ₂] ⁼ , [PdCl ₂ (Me ₂ S) ₂], [Pd(salicylaldoxim) ₂], etc. |
| 45 | [Ag(picolinic acid) ₂]. |
| 76 | [PtCl ₄] ⁼ , [Pt(NH ₃) ₄] ⁺⁺ , [Pt en ₂] ⁺⁺ , [Pt(S ₂ C ₂ O ₂) ₂] ⁼ , [PtX ₂ (R ₂ S) ₂], [PtX ₂ (R ₃ P) ₂], [PtX ₂ (R ₃ As) ₂], [PtX ₂ (R ₃ Sb) ₂], [Pt(CN) ₄] ⁼ , [AuCl ₄] ⁻ , [AuBr ₄] ⁻ , etc. |

The fact that complexes of bivalent nickel, palladium and platinum occupy the great majority of planar compounds suggests the stability of these complexes. A remarkable regularity is found among the effective atomic numbers of their central ions.

6) E. G. Cox and K. C. Webster, *Z. Krist.*, **90**, 561 (1935).

Table X.

| Effect. at. no. | Stable planar complex | Electronic configuration | | |
|-----------------|--|--------------------------|---------|---------------------|
| | | Inert-gas kernel | d-Shell | Co-ordination level |
| 26 | [Ni(CN) ₄] ²⁻ | 18(A) | 4 | 4 |
| 44 | [Pd(NH ₃) ₄] ²⁺ | 36(Kr) | 4 | 4 |
| 76 | [PtCl ₄] ²⁻ | 68(Lu ³⁺) | 4 | 4 |

Here again holds the assumption that the electronic configuration in the d-shell of a complex has a similar symmetry to its external configuration. Four d-electrons, therefore, must belong to one and the same Stoner grouplet, i.e., in *d_x* and *d_y*.

Electronic Configuration and Magnetism.

It is now possible to predict the configuration of ions and molecules if their composition is known. At the same time the electronic configuration of the co-ordination level can be decided, by postulating that the co-ordination functions could not be of different principal quantum numbers. Examples for typical elements are shown in Table XI.

Table XI.

| Ion or molecule | 1s | 2s 2p _x 2p _y 2p _z | 3s 3p _x 3p _y 3p _z 3d _x 3d _y 3d _{xy} 3d _{yz} 3d _{zx} |
|--|----------------------------|--|---|
| BeO ₂ ²⁻ , BO ₂ ⁻ | 2 | [2 2] | |
| BO ₃ ³⁻ , CO ₃ ²⁻ , NO ₃ ⁻ , BCl ₃ | 2 | [2 2 2] | |
| BF ₄ ⁻ , BeF ₄ ²⁻ , CCl ₄ , NH ₄ ⁺ | 2 | [2 2 2 2] | |
| NO ₂ ⁻ | 2 | [2 2 2] | |
| NH ₃ , OH ₄ ⁺ | 2 | [2 2 2 2] | |
| OH ₂ | 2 | [2 2 2 2] | |
| SiO ₄ ⁴⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ , ClO ₄ ⁻ | 2 | 2 2 2 2 | [2 2 2 2] |
| PO ₃ ³⁻ , SO ₃ ²⁻ , ClO ₃ ⁻ | 2 | 2 2 2 2 | [2 2 2 2] |
| SO ₂ , AlCl ₃ | 2 | 2 2 2 2 | [2 2 2] |
| SO ₂ | 2 | 2 2 2 2 | [2 2 2] |
| ClO ₂ ⁻ | 2 | 2 2 2 2 | [2 2 2 2] |
| SF ₆ , [SiF ₆] ²⁻ , [AlF ₆] ³⁻ | 2 | 2 2 2 2 | [2 2 2 2 2 2] |
| 2 | co-ordinated electron pair | | [2 2 2 2] tetrahedral quantization |
| [2 2] | digonal quantization | | [2 2 2 2 2 2] octahedral quantization |
| [2 2 2] | trigonal quantization | | |

The electron distribution in compounds of transition elements can be decided as well, if a few assumptions are allowed for d-electrons. As has been stated above, two pairs of d-electrons are assumed to promote to the co-ordination level

in the planar quantization and a similar case is assumed for compounds of nine-functioned co-ordination. As regards the electrons left in unsaturated *d*-shells, are invoked the following assumptions. Since the distribution of such electrons must naturally be affected by the configuration of the co-ordination sphere, it is postulated that they are distributed in orbitals arranged after the symmetry of the external configuration, that is, the *d*-electrons occupy first the Stoner grouplet of six or four according as the external configuration is octahedral or planar, Sidgwick's grouplet rule⁷⁾ being assumed. The electronic configuration in compounds of transition elements of the first series are as follows.

Table XII.

| Ion or Molecule | 1s-3p | 3d _x 3d _y | 3d _{xy} 3d _{yz} 3d _{zx} | 4s 4p _x 4p _y 4p _z 4d _x 4d _y |
|---|----------------|---------------------------------|--|--|
| TiO ₄ ⁴⁻ , VO ₃ ³⁻ , CrO ₄ ²⁻ , MnO ₄ ⁻ | 18 | | | <u>2 2 2 2</u> |
| [Cr(NH ₃) ₆] ³⁺ , [Cr(CN) ₆] ³⁻ | 18 | | 1 1 1 | <u>2 2 2 2 2 2</u> |
| [Fe(CN) ₆] ³⁻ | 18 | | 2 2 1 | <u>2 2 2 2 2 2</u> |
| [Fe(CN) ₆] ⁴⁻ , [Cr(NH ₃) ₆] ³⁺ | 18 | | 2 2 2 | <u>2 2 2 2 2 2</u> |
| [Cu(NH ₃) ₄] ⁺⁺ | 18 | 2 2 | 1 | <u>2 2 2 2 2 2</u> |
| [Ni(CN) ₄] ⁻ | 18 | 2 2 | | <u>2 2 2 2 2 2</u> |
| Ni(CO) ₄ | 18 | 2 2 | 2 2 2 | <u>2 2 2 2</u> |
| [Ni(NH ₃) ₆] ⁺⁺ | 18 | 1 1 | 2 2 2 | <u>2 2 2 2 2 2</u> |
| [Zn(H ₂ O) ₆] ⁺⁺ | 18 | 2 2 | 2 2 2 | <u>2 2 2 2 2 2</u> |
| | 2 | co-ordinated electron pair | | <u>2 2 2 2 2 2</u> planar quantization |
| | <u>2 2 2 2</u> | tetrahedral quantization | | <u>2 2 2 2 2 2</u> octahedral quantization |

The electronic configuration in compounds of transition elements of the third series is as follows.

Table XIII.

| Ion or molecule | 1s-5p | 5d _x 5d _y | 5d _{xy} 5d _{yz} 5d _{zx} | 6s 6p _x 6p _y 6p _z 6d _x 6d _y 6d _z 6d _{xy} 6d _{yz} |
|--|-------|---------------------------------|--|--|
| ReO ₄ ⁻ | 68 | | | <u>2 2 2 2</u> |
| OsF ₈ | 68 | | | <u>2 2 2 2 2 2 2 2</u> |
| [W(CN) ₆] ⁴⁻ | 68 | | | <u>2 2 2 2 2 2 2 2</u> |
| [PtCl ₆] ⁻ | 68 | | 2 2 2 | <u>2 2 2 2 2 2</u> |
| [Pt(NH ₃) ₂ Cl ₂] | 68 | 2 2 | | <u>2 2 2 2 2 2</u> |
| [AuBr ₄] ⁻ | 68 | 2 2 | | <u>2 2 2 2 2 2</u> |
| HgCl ₂ | 68 | 2 2 | 2 2 2 | <u>2 2</u> |
| | | | | <u>2 2 2 2 2 2 2 2</u> cubic quantization |
| | | | | <u>2 2 2 2 2 2 2 2 2</u> nine-functioned quantization |

From the electronic distribution can be predicted the magnetic property of

7) N. V. Sidgwick, 'The electronic theory of valency', pp. 204-18, London, 1929.

various compounds. Of the compounds in Table XII and XIII, the following four are paramagnetic and all others diamagnetic.

Table XIV.

| Compound | Predicted number of unpaired electrons | Predicted Bohr magnetons | Observed Bohr magnetons |
|---|--|--------------------------|-------------------------|
| $[\text{Cr}(\text{NH}_3)_6]\text{I}_3$ | 3 | 3.87 | 3.60 |
| $[\text{Cr}(\text{CN})_6]\text{K}_3$ | 3 | 3.87 | 3.91 |
| $[\text{Ni}(\text{NH}_3)_6]\text{Br}_2$ | 2 | 2.83 | 3.03 |
| $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$ | 1 | 1.73 | 1.85 |

As can be seen the prediction coincides with the observation in all the cases, even for compounds which contradict the Welo-Baudisch rule.⁸⁾ For example $[\text{Ni}(\text{CN})_4]^-$, $[\text{AuBr}_4]^-$ and $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ have 34, 84 and 84 electrons respectively around the co-ordination center, and paramagnetism is expected from the Welo-Baudisch rule. These compounds are, however, diamagnetic as can be predicted by the present theory. The magnetic property of compounds of transition elements will be dealt with in detail on another opportunity.

Co-ordination Theory and Absorption Spectra.

Absorption spectra of co-ordination compounds generally consist of absorption bands of three kinds. One of the present authors^{9,10)} has come to the conclusion that the first band is due to electron transition in unsaturated *d*-shells. A compound whose *d*-shell is either empty or full, does not give rise to the first band^{10,11)}. The second band is attributed to co-ordination electrons.^{11,12,17)} Since, from the viewpoint of the present co-ordination theory, all the compounds, organic as well as inorganic, are co-ordination compounds, they must have the second band. An example of application of the co-ordination theory to absorption spectra of organic compounds has already been shown.¹³⁾ The present author has also found that the third band is due to neutralization between the central cation and the ligand anion and appears when a pair or pairs of negative radicals are

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- 8) L. A. Welo and O. Baudisch, *Nature*, 116, 359, 606 (1925).
 - 9) R. Tsuchida, *Bull. Chem. Soc. Japan*, 13, 388 (1938).
 - 10) R. Tsuchida, *J. Chem. Soc. Japan*, 59, 731 (1938).
 - 11) S. Kashimoto and R. Tsuchida, *J. Chem. Soc. Japan*, 60, 347 (1939).
 - 12) R. Tsuchida, *J. Chem. Soc. Japan*, 59, 819 (1938).
 - 13) R. Tsuchida and T. Tsumaki, *Bull. Chem. Soc. Japan*, 13, 527 (1938).
 - 14) R. Tsuchida, *Bull. Chem. Soc. Japan*, 13, 436 (1938).
 - 15) R. Tsuchida, *J. Chem. Soc. Japan*, 59, 731 (1938).
 - 16) R. Tsuchida and S. Kashimoto, *Bull. Chem. Soc. Japan*, 11, 785 (1936).
 - 17) H. Kurova and R. Tsuchida, *J. Chem. Soc. Japan*, 59, 1142 (1938).

co-ordinated in trans-positions of an octahedral or planar complex.¹⁵⁾¹⁶⁾ The fact that negative radicals co-ordinated in trans-positions give rise to the third band may be explained in terms of the eigenfunctions in the octahedral quantization, in which bonds in trans-directions are closely related with each other through p -functions while bonds in cis-positions are less closely connected. In the tetrahedral quantization, however, all the bond functions are equally related with one another and such compounds have always the third band. As an example may be cited chromate ion which has the third band along with the second.¹⁸⁾ Detailed discussion on the relation between absorption spectra and eigenfunctions will be reported later.

Summary.

(1) The zeroth order eigenfunctions for the formation of compounds of various co-ordination numbers are given.

(2) It has been shown that the octahedral bond is the strongest of all the co-ordination bonds.

(3) The method of finding the configuration of compounds of typical and transition elements has been reported.

(4) The composition alone of an ion or molecule of any element being given, the electronic distribution, the magnetic moment as well as the external configuration can be predicted in satisfactory coincidence with the observed data.

(5) The relation between the configuration and the absorption spectrum has been referred to.

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18) R. Tsuchida and M. Kobayashi, *Bull. Chem. Soc. Japan*, 13, 471 (1938).