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Topological Ligand Design. II. The Definition and Derivation of Extended and Complex Ligand Graphs*

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An extended ligand graph is a set of several points corresponding to donor atoms, where each pair of points is connected by *n* lines when these atoms are able to form *n* chelate rings with a metal ion. These graphs can cover all the ligands, but they may not express the geometrical patterns of some complicated ligands clearely enough for them to be discriminated. A complex ligand graph is a set of some main points and sub-points connected by sub-lines, where the main points, sub-points, and sub-lines correspond to donor atoms, carbon atoms forming chelate bonds, and chemical bonds among them respectively. All the complex ligand graphs can then be systematically derived from donor-atomic graphs, which are composed of only main points and main lines and are equivalent to the simple ligand graphs previously designed. Another designing method of ligands is proposed for a certain coordination sturcture. A complex ligand graph to which no more sub-points or sub-lines can be added is called a parent ligand graph. Then all the complex ligand graphs for such a coordination are derived from the parent ligand graphs by neglecting some sub-points or by removing some sub-lines successively.

In the previous paper[1)] a simple ligand graph was defined and all of the lower members were systematically derived. This is one of the most useful methods for designing and classifying ligands and can bring us various information about future ligands. However, it cannot cover some kinds of ligands containing special kinds of branched carbon atoms, where branches form their several chelate rings with a metal ion, since any branch point in a simple ligand graph should be not a carbon atom, but a donor atom. To cover these complicated ligands, the definition of the ligand graph must be further extended.

Theoretical

Extended Ligand Graph. An "extended ligand graph" is a set of several points corresponding to donor atoms, where each pair of points is connected by *n* lines when these atoms are able to form *n* chelate rings with a metal ion. For example, a complicated terdentate ligand (A) in Fig. 1 is expressed by the

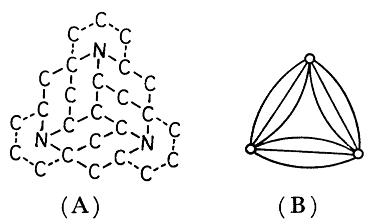

Fig. 1. An example of the extended ligand graph. (A): Ligand, (B): its extended ligand graph.

extended ligand graph (B); some carbon chains connected by broken lines are neglected in this graph, because they cannot become the chelate ring. Therefore, branched carbon atoms may be commonly used for different chelate rings. These extended ligand graphs may contain some double or triple lines; the maximum degree of their points is nine, since every pair of points may have triple lines. They can represent all the chelate ligands and can be derived systematically

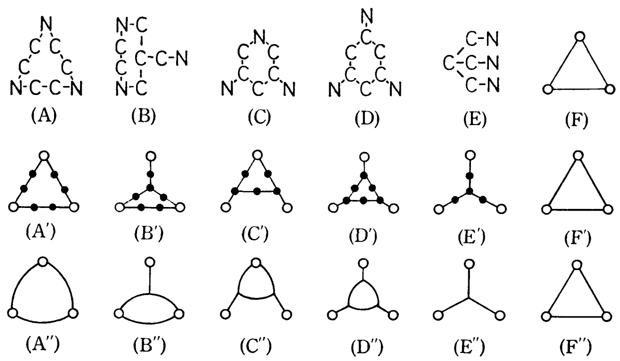

Fig. 2. Various graph expressions for some ligands. (A) to (E): ligands, (F): their extended ligand graph, (A′) to (E′): their several complex ligand graphs, (A″) to (E″): their several complex pattern graphs, (F′) and (F″): their composite pattern and donor-atomic graph.

from the simple ligand graphs by substituting some of their lines for double or triple lines. However, they do not express the geometrical patterns of complicated ligands well enough for them to be discriminated. For example, the ligands from (A) to (E) in Fig. 2 are expressed by the same extended ligand graph (F). In order to correct this defect, a complex graph should be applied which is a set of main points and main lines, with each main line also a graph composed of sub-points and sub-lines.

Complex Ligand Graph. A "complex ligand graph" is a set of several main points and sub-points connected by sub-lines, where the main points, sub-points, and sub-lines correspond to donor atoms, carbon atoms forming chelate bonds, and chemical bonds among these atoms respectively. Examples of the complex ligand graphs are shown as (A′) to (E′) in Fig. 2. The degree of the main points does not exceed three, while that of the sub-points is only two or three, since no carbon atom can be an end-point. The complex ligand graph contains neither multiple sub-lines nor self-loops, and is naturally a connected planar graph as well as a simple ligand graph.

On the complex ligand graph, a graph-theoretical path between two main points containing only two

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or three sub-points is called a "chelate path." For example, every N–C–C–N or N–C–C–C–N chain of the ligands in Fig. 1 or Fig. 2 is a chelate path. Accordingly, each line on an extended ligand graph corresponds to a chelate path. Every main point is a common terminal point of a maximum of nine chelate paths; this is obvious from the maximum degree of the points in the extended ligand graph. Every sub-point belongs to one, two, or three chelate paths.

When all the sub-points of degree two are neglected in a complex ligand graph, what is left is called a "complex pattern graph" and its lines are called a "series"; these definitions are equivalent to those in the simple ligand graph. Some examples are shown in Fig. 2, (A″) to (E″).

Then new terms are defined in order to derive these complex graphs from some simpler, non-complex graphs which have already been designed. When a pair of main points have at least one chelate path, they are connected by a "main line," while a set of several main points connected by several main lines is called a "donor-atomic graph," which is quite equivalent to the simple ligand graph, since it has neither sub-points, sub-line, multiple-line, nor self-loop. As the main line is not related to the number of the chelate paths or the branched carbon atoms contained in it, all the ligands in Figs. 1 and 2 can be represented by the same trigonal-shaped donor-atomic graph, as is shown in Fig. 2 (F″).

When several chelate paths between each pair of main points in a complex pattern graph are observed, there are four kinds of simple patterns (shown in Fig. 3) as far as ligands for five- or six-membered chelate rings are concerned; they are called "unit patterns." The (A), (B), (C), and (D) unit patterns contain one, two, two, and three chelate paths respectively.

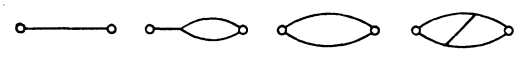

Fig. 3. Unit patterns.

When each main line of a donor-atomic graph is displaced by one of the unit graphs, the complex graph thus produced is called a "composite pattern." As each main line in the complicate ligand in Fig. 1 contains three chelate paths, for example, the composite pattern for this ligand is obtained by displacing three main lines by the unit pattern (D) in Fig. 3. For the ligands from (A) to (E) in Fig. 2, their composite patterns are represented by the same trigonal graph (F′), which is identical to their donor-atomic graph (F″), since every main line contains only one chelate path; its unit pattern is the same as (A) in Fig. 3.

A composite pattern is not always identical to its complex pattern graph, for two adjacent unit patterns have some common sub-lines and sub-points. For example, all the ligands in Fig. 2 have the same composite pattern (F′); however, they are represented by several complex pattern graphs, (A″) to (E″), because they have different parts in common. In

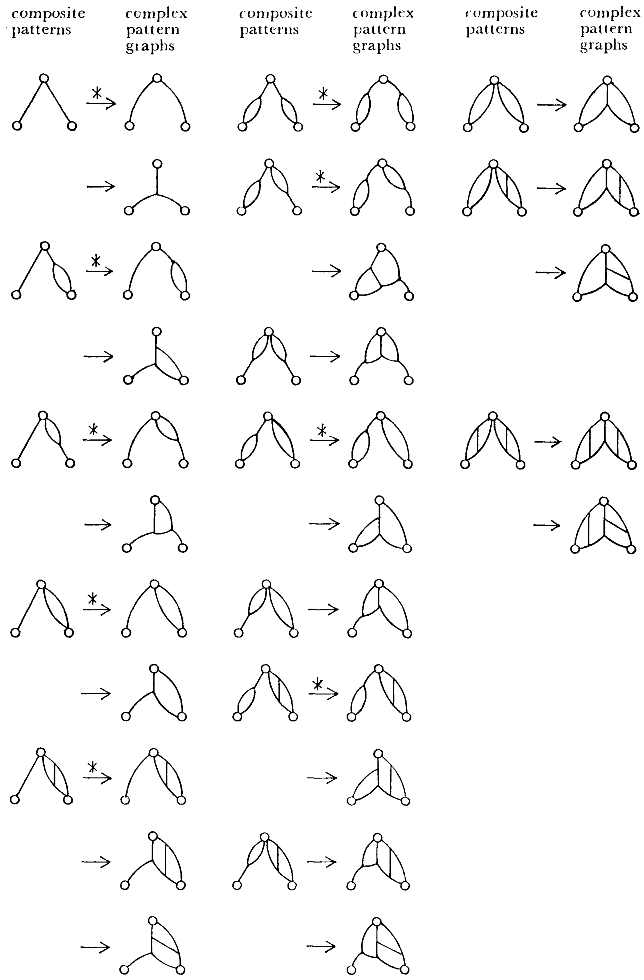

Fig. 4. Condensations between two unit patterns. *: Without condensation.

these complex pattern graphs in Fig. 2, the common parts of the unit patterns are expressed by straight lines, and the others, by curved lines.

Thus, a new concept of "condensation" should be introduced; it means a partial fusing of two patterns, as when the condensation of two benzene rings produces a naphthalene frame. All the condensations between a pair of adjacent unit patterns are summarized in Fig. 4. By various combinations of four kinds of unit patterns, many composite patterns are obtained from a donor-atomic graph, and by various condensations among the unit patterns, further, more complex pattern graphs are obtained. The condensation is not always necessary, but if the degree of a main point exceeds three in a composite pattern, the condensation must not be neglected.

Finally, the complex ligand graphs can be derived by allotting some sub-points of degree two to some series of a complex pattern graph, so that each chelate path may have two or three sub-points. Thus, all the complex ligand graphs can be obtained systematically from the donor-atomic graphs, which have already been designed.

On the contrary, any ligands can be reduced to their donor-atomic graphs. For example, a complicated quadridentate ligand (A) in Fig. 5 is represented

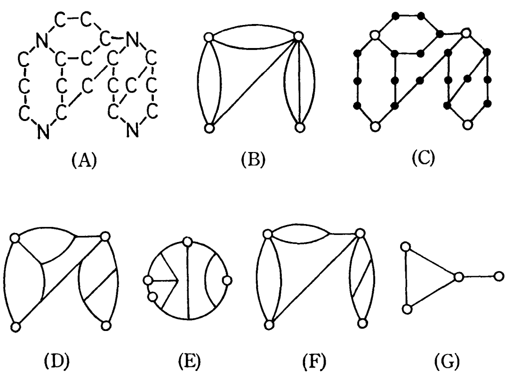

Fig. 5. Reduction of a ligand structure into its donor-atomic graph. (A): Ligand, (B): extended ligand graph, (C): complex ligand graph, (D): complex pattern graph, (E): its schematical illustration, (F): composite pattern, (G): donor-atomic graph.

by both the extended ligand graph (B) and the complex ligand graph (C). Then, (C) is reduced to the complex pattern graph (D) by neglecting all the sub-points of degree two. (E) is a schematical illustration of (D). When all the condensed chelate paths in (D) are separated into the unit patterns, its composite pattern (F) is obtained. Finally, (F) is reduced to its donor-atomic graph (G) by substituting each unit graph for a main line.

Ligand Design for a Certain Coordination Structure. The above derivation method for the complex ligand graphs is sufficiently systematic and can cover all of these graphs, but a ligand graph derived mechanically cannot always fit a special coordination structure, and in a computer manipulation it is not easy to select them. Furthermore, one often needs knowledge about all the ligands for a special coordination, such as octahedral, tetrahedral, or square planar.

When all the donor-atomic graphs which are fit for such special coordination are found, all the composite patterns, complex pattern graphs, and complex ligand graphs may be derived successively. The donor-atomic graphs for any planar coordinations are always only linear or circular graphs, while those for tetrahedral or octahedral coordination are equivalent to all the simple ligand graphs with $m=4$ or $m=6$, as was illustrated in Table 3 in the previous paper.[1] Therefore, all the ligands for such purposes may be designed by the above-described procedure, but they may still contain some useless ligands which cannot coordinate to a metal ion easily because of intricate carbon-chains. Therefore, an alternate designing method for these complex ligand graphs will be proposed.

In a certain coordination structure, a complex ligand graph to which no more sub-points or sub-lines can be added, *i.e.*, a high density complex graph, is called a "parent ligand graph." Several kinds of parent ligand graphs may exist in each coordination structure. If all of them are found, all the complex ligand graphs for such a coordination can be derived as their "daughter ligand graphs" by neglecting some sub-points or removing some sub-lines.

Planar Coordinations: The donor-atomic graph of the parent ligand graphs for an n-polygonal planar co-

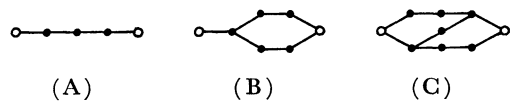

Fig. 6. Linear unit graphs.

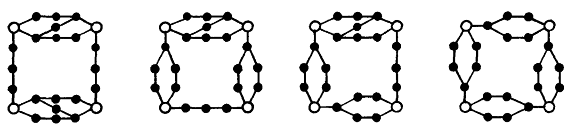

Fig. 7. Parent ligand graphs for the square planar coordination.

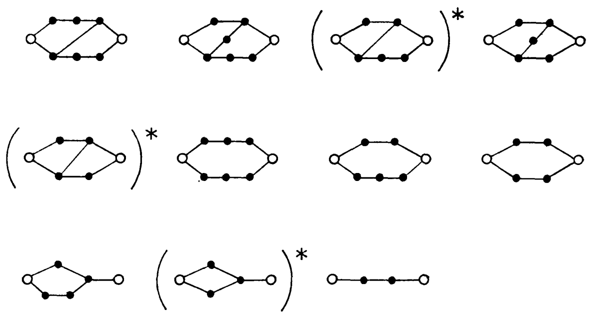

Fig. 8. Daughter unit graphs for the planar coordination. *: Omitted here because of containing less than five-membered ring.

ordination is an n-polygonal graph. These parent ligand graphs are, then, obtained by displacing each edge of the n-polygon with one of the three "linear unit graphs" shown in Fig. 6. This procedure is similar to that used in deriving the composite patterns, but these unit graphs contain three sub-points of degree two or three on each chelate path. In this case, the condensation between two unit graphs would not occur, since two unit graphs surrounding a metal ion cannot approach each other so closely. For example, all the parent ligand graphs for the square planar coordination can be obtained by the combination of four unit graphs, so that every main point may have degree three as is shown in Fig. 7.

In order to derive the daughter ligand graphs, all the "daughter unit graphs" of three unit graphs are found by neglecting sub-points or removing sub-lines from the unit graphs, as is shown in Fig. 8. Then a circular daughter ligand graph might be derived by substituting each edge of the n-polygon for one of those daughter unit graphs. All the linear daughter ligand graphs are derived by removing one unit graph or one daughter unit graph from those circular daughter ligand graphs and parent ligand graphs.

Polyhedral Coordinations: An m-polyhedron is covered with mn-polygons (sometimes different polygons). Then its parent ligand graphs are obtained when every surface is covered by n-polygonal unit graphs, with condensations on some edges. As a popular example, a tetrahedron or an octahedron is covered with four or eight equilateral triangles. The parent ligand graphs for such coordination are derived by covering all surfaces with five kinds of trigonal unit graphs, as is shown in Fig. 9.

The adjacency of two trigonal unit graphs is geo-

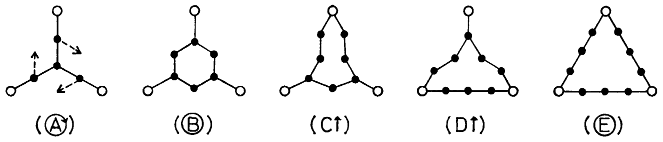

Fig. 9. Trigonal unit graphs.

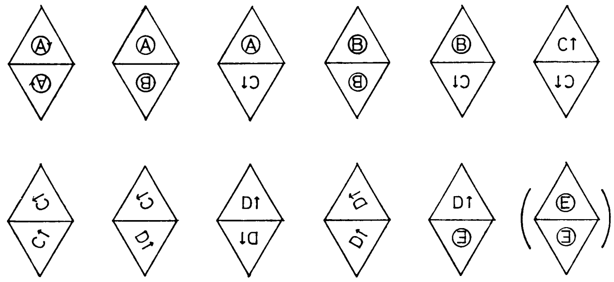

Fig. 10. Adjacency of two trigonal unit graphs.

metrically restricted. Every edge of the (A), (B), or (E) unit graph in Fig. 9 is equivalent by symmetry, but (C) or (D) has two kinds of edges. When two (A) graphs are adjacent, new sub-point and sub-lines are added along the arrow. The two rotational isomers of (A) were neglected here. All the possible geometries for a pair of adjacent unit graphs are shown in Fig. 10. As the unit graph (E) has less density, it can be used for the parent ligand graph only when it is surrounded with three unit graphs (D). Therefore, (E)-(E) adjacency is of no use, although possible geometrically.

Under these conditions, nine parent ligand graphs for the tetrahedral coordination are obtained, as is shown in the development diagrams in Fig. 11. They all have quite rigid cage structures in spite of being composed of three-membered carbon chains. If their metal chelates could ever be prepared, the cations would be spherical with a extreme stability and quite a hydrophobic nature.

Similar procedures can be applied to other polyhedral

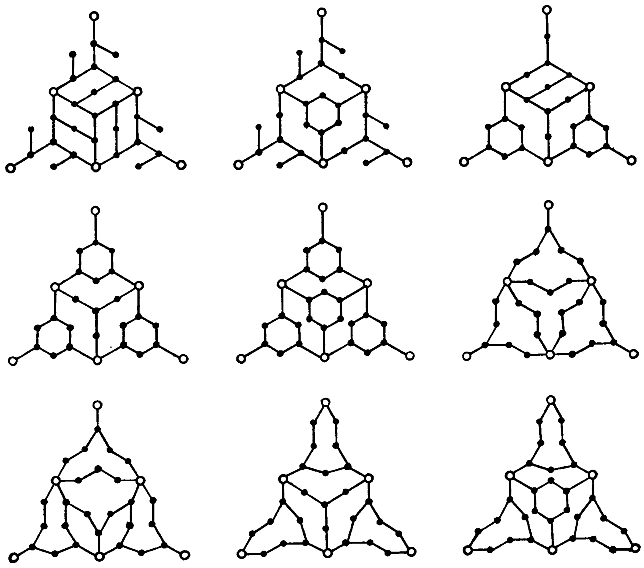

Fig. 11. Parent ligand graphs for the tetrahedral coordination.

coordinations covered by any polygons other than a triangle when proper unit graphs for such polygon have been constructed. Furthermore, this method is also applicable to the polynuclear coordinations, since they are considered to be combined polyhedral coordinations.

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Reference

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