Symmetry properties of chemical graphs VIII.
On complementarity of isomerization modes[*]

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Isomerization mode defines the process of interconversion of one isomer into another. Several mechanisms are conceivable for degenerate rearrangements and, in general, lead to a distinctive network of relations between participating isomers. Here we consider selected modes which are complementary in the sense that if mode 1 transforms an isomer A into B, C, D etc., then mode 2 transforms the same isomer A into X, Y, Z, etc., which includes all isomers not comprised by the first mode. Physico-chemical complementarity can be translated into mathematical complementarity of associated chemical graphs. This allows us to use the tool of Graph Theory. One example of graph theoretical use is the theorem that graph G and its complement $\bar{G}$ have the same automorphism group (i.e., the same symmetry). We have shown that a close examination of a graph and its complement and their components allows us to recognize the automorphism group in some complex cases without resorting to canonical numbering or other involved procedures, and even allows us to determine isomorphism of different processes.

Key words: Graph theory—chemical graphs—degenerate rearrangements—isomerization of octahedral XY_6 complexes—isomerization of tetragonal-pyramidal XY_4 complexes

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1. Introduction

Graph Theory studies the combinatorial and topological content of relations and has an important advantage over usual algebraic approaches, in that it not only permits an analytical approach, but it also offers pictorial representation of frequently complex situations. Combinatorial complexity of many chemical transformations soon becomes overwhelming when the size of structures and valencies of atom increase. There are only two isomers for tetravalent carbon structure with asymmetric substitution (i.e. d and l isomers); there are 20 isomers for pentavalent trigonal bipyramidal structure XY_5 if the ligands are distinguishable, and there are 30 isomers in case of hexavalent octahedral XY_6 with six different ligands. Representation of isomerizations with graphs was suggested some 15 years ago [1] and such a novel approach has been quickly recognized as an important advance for the study of rearrangements. Besides its obvious advantage of allowing visualization of rather complex relations, the introduced graphs of chemical transformations have lead to the recognition that apparently different chemical processes may have a same underlying mechanism. Thus the charge shift in $CH_3CH_2^+$, a topic of organic chemistry, from the graph theoretical perspectives is found to be equivalent to interconversion of trigonal bipyramidal complex XY_5, an inorganic chemistry topic.

In this communication we will illustrate additional novel examples that allow one to recognize related processes. We will be interested here in determining the symmetry of selected graphs (or in graph theoretical terminology [2], determining the automorphism group of a graph). In particular, we will consider relations between a graph G and its complement $\bar{G}$, which is defined [3] as a graph with the same set of vertices and the connections only between those vertices which are not connected in G. (For the reader's convenience we have collected in the Appendix a glossary of graph theoretical terms used). In Fig. 1 we show a graph of a trigonal prism and its complement, a six-membered cycle. A graph G and its complement $\bar{G}$ have the same group [4]. This important theorem has some practical use, because one of the two graphs, G or $\bar{G}$, may be simpler for analysis. For instance, all vertices in the six-membered cycle of Fig. 1 are obviously equivalent, therefore all six vertices of the trigonal prism are equivalent. While the former can be depicted so that equivalence is evident, this is not possible for a two dimensional projection of the latter; however, because the graph is simple, the equivalence of all vertices is easy to recognize. In more complex graphs (to be examined later) advantages of the above approach will be more clear. The significance of the complementarity of graphs for physico-chemical studies arises from the observation that selected isomerization modes are complementary [5]. For example, digonal twist in the octahedral complexes considered by Gielen [6] and Muetterties [7] is complementary to rhombic twist considered by Ray and Dutt [8]. Thus, two isomers connected by digonal twist are excluded in direct transformation in the rhombic twist and *vice versa*. The corresponding graphs for the two mechanisms, the digonal twist and the rhombic twist, are shown in Fig. 2. From the graphic representations, taken from Ref. [5], it is not apparent, without referring to vertex labels, that the graphs are related as a complementary
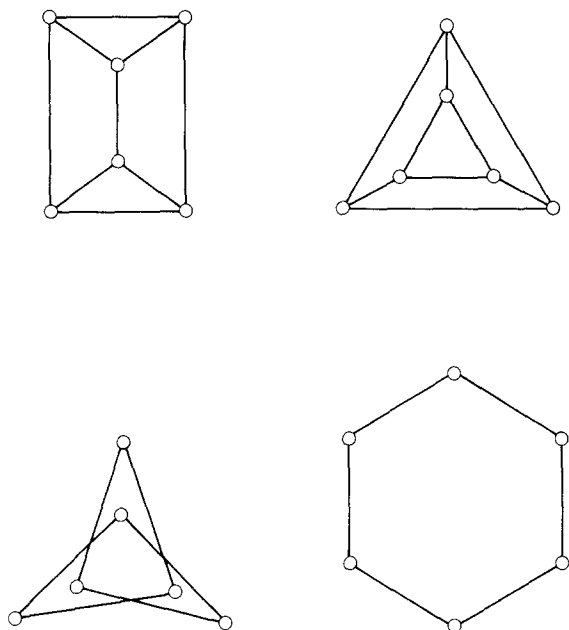
Fig. 1. Graph representing trigonal pyramid in two alternative pictorial forms and its complement, a six-membered cycle

pair. Of course, from one of the graphs, the other can be constructed, but if the other graph appears in another study and is not suspected to be related, we face the difficult task of recognizing the graph as a complement of some existing (familiar) graph. We will here, by considering the symmetry of graphs, direct ourselves to that task.

2. Isomerization of octahedral complexes

Recently we have considered the problem of isomerization of octahedral complexes *via* digonal twist mechanism, which produces graph G, at bottom in Fig. 2 [9]. The symmetry of the graph G has previously been established as S_6, on the basis of outer isomorphism of two- and six-digit labels [10], as well as from the fact that the graph represents a complement of $L(K_5)$, the *line graph* of K_5, which can be readily verified once S_6 is *suspected* as the automorphism group [11, 12]. The *line graph* $L(G)$ of a simple graph G is the graph whose vertices are in one-one correspondence with the edges of G, two vertices of $L(G)$ being adjacent if and only if the corresponding edges of G are adjacent [3]. Furthermore, use of canonical labels [13] and orbits derived from the adjacency matrix [14] revealed cycle structure for permutations, and finally, canonical labels were used to list representative symmetry elements as selected permutations of vertex labels [9]. However, from the fact that graph G is the complement of the graph representing

the rhombic twist mechanism, solving one problem constitutes the basis for the solution of the other. From the theorem that G and $\bar{G}$ have the same symmetry, we immediately conclude that the graph representing rhombic twist as a mechanism for isomerization of octahedral complexes also has the same symmetry, S_6. But the graphs are different and the correspondence between arbitrary labels and symmetry permutations has to be established if representative elements are to be listed. On the other hand, we need not know the relationship between a new graph, $\bar{G}$, representing rhombic twist mode, and the old graph, G, or any other graph to which $\bar{G}$ could be related. We should therefore focus our attention on graph $\bar{G}$ and try to use its properties in order to detect its relation to other more familiar graphs. We will outline such a search for useful properties and will avoid
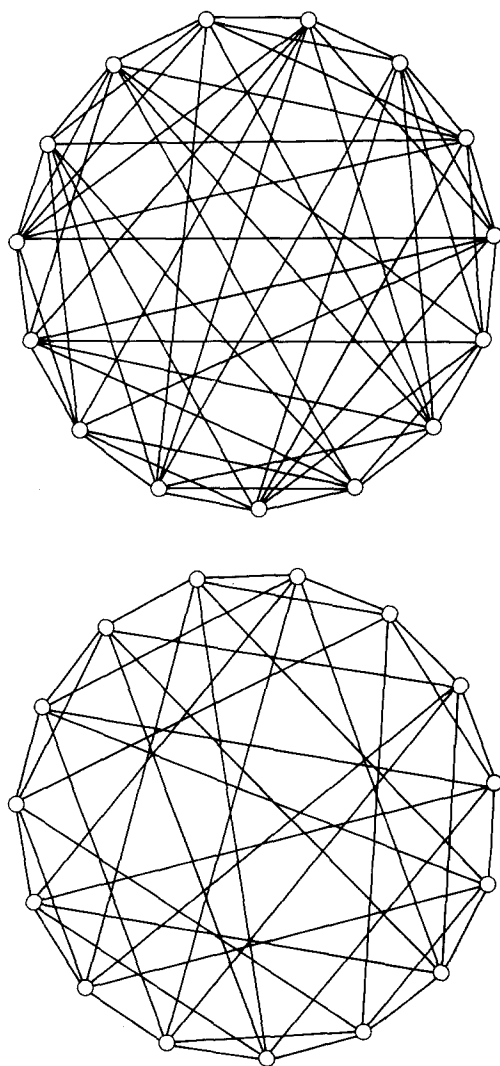
Fig. 2. Graph representing isomerization of octahedral complexes with the digonal twist rearrangement mode (bottom) and graph representing isomerization of the same complexes under the rhombic trist mode (top), as shown by Balaban [5]

the use of canonical labels, which offer a general method but at the cost of a somewhat difficult search for canonical labels. Instead of canonical labels, we will examine various subgraphs and will see how they facilitate the determination of automorphism and isomorphism for selected graphs.

Let's examine graph $\bar{G}$ of Fig. 2 more carefully. We find numerous triangles (subgraphs K_3), tetrahedra (subgraphs K_4) and even "four dimensional tetrahedra", simplexes K_5. One such K_5 subgraph is shown in Fig. 3 with its vertices labeled as A, B, C, D, and E. Let's label the remainder of vertices with the same letters A–E following the rule: a vertex receives labels of those vertices in K_5 subgraph to which it is connected. One finds that each of the remaining vertices has only two neighbors in K_5, hence the remaining ten vertices of the graph $\bar{G}$ will each receive a two letter symbol. Already this finding suggests a more symmetrical pitctorial representation of our graph $\bar{G}$. We can draw K_5 as a symmetrical pentagram (vertices at the periphery in Fig. 4) and place ten additional vertices inside K_5 periphery to produce a regular polygon. For a better visibility alternative vertices have been slightly displaced towards the center of the figure. Since *each* line in K_5 is defined by two vertices and can be associated with a *pair* of labels we see that the remainder of the graph is in fact the line graph of K_5, and the two components of $\bar{G}$, K_5 and $L(K_5)$, are connected whenever a same label occurs. As the result we obtain a more symmetrical pictorial form of G shown in Fig. 4, showing as the apparent symmetry D_{5h}. This represents a relatively highly symmetrical image of the graph considered. Construction of alternative pictorial forms for graphs is important, because nontrivially related
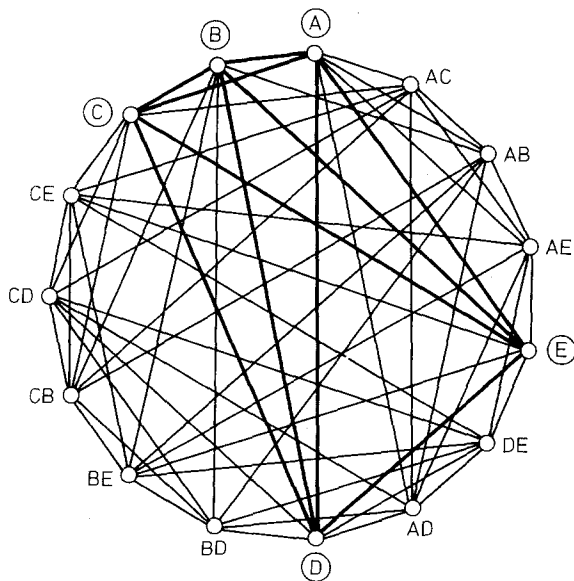

Fig. 3. The graph representing the rhombic twist mechanism of Fig. 2 with one of its K_5 subgraphs emphasized (labels A–E). The remaining vertices received *two* labels depending on which of A–E vertices are their neighbors

novel forms may reveal some new structural aspects of the processes described by a graph. This point has been illustrated by Dunitz and Prelog [15] for the Petersen graph, which depicts an isomerization mode of trigonal bipyramidal XY_5 complexes. They drew attention to an alternative form for the graph based on a regular pentagonal pattern familiar in mathematical literature [16], and a novel tetrahedral form, in contrast to trigonal forms customary in chemistry. There are, however, no simple rules for construction of alternative forms for graphs; for the most part it is a trial and error approach. It is useful to know about the presence of Hamiltonian circuits, and in particular to know the symmetry of the graph when considering alternative pictorial diagrams for a given graph. In addition, as just demonstrated, examination of highly symmetrical subgraphs, such as K_5 in this case, can also facilitate the search for alternative graphical illustrations of the considered relations.

3. Examination of selected subgraphs

"The problem of finding alternative pictorial forms" for a graph involves, both the topological and the combinatorial components of graphs. The former is reflected in the search for sites of the vertices; the latter involves labeling of vertices and implied connections, which, even if vertices were placed in very symmetrical locations, need not produce a symmetrical pattern unless compatible labeling can be found. An exhaustive search for assignment of labels is out of question, once the sites for the vertices has been selected. Instead of taking a trial-and-error approach, we advocate here "an educated guess" approach. This is, in essence, a constrained trial-and-error scheme, and is more likely to be productive. The basis for our guesses are selected properties of graphs considered, in particular the presence of subgraphs that are already familiar from other studies. Such subgraphs may suggest in the first place how to select a particular geometrical pattern among many nontrivially related patterns for the vertices location.

Let's examine graph G, describing the digonal twist mode of octahedral complexes, of which $\bar{G}$ is the complement. In Fig. 5 we show a number of symmetrical subgraphs which one can identify within G. The particular examples constitute disjoint subgraphs pairwise (one pair is shown at the top of Fig. 5 with the partitioning of vertices into $8+7$; the other pair is shown at the bottom of the Fig. 5 with the corresponding partitioning $9+6$). Other such disjoint subgraphs are possible, like partitioning $12+3$, in which one component is a triangle K_3. The subgraph having nine vertices (Fig. 5), known as a simplex-polycorypha bounded by six pentahedra [17], appears in the description of a degenerate isomerization of $XY_3XY_2XY_3$ molecules [18]. Thus interestingly, we find that apparently unrelated problems – the digonal twist in octahedral complexes and isomerization in propane-type molecules, under relative rotation of the XY_3 end groups – have something in common!

The number of components and subgraphs in complex graphs itself is large and one should restrict attention to the subgraphs which constitute components (i.e.
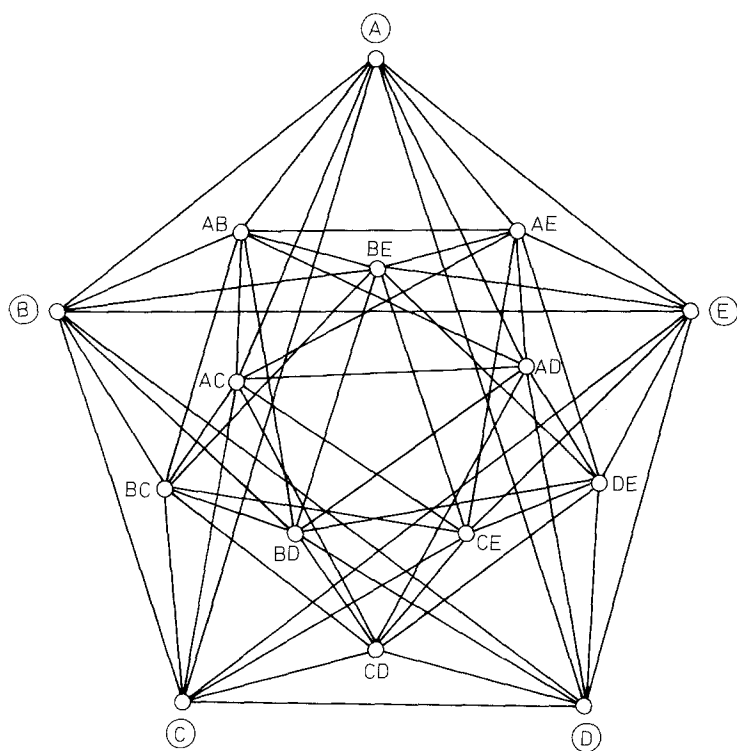
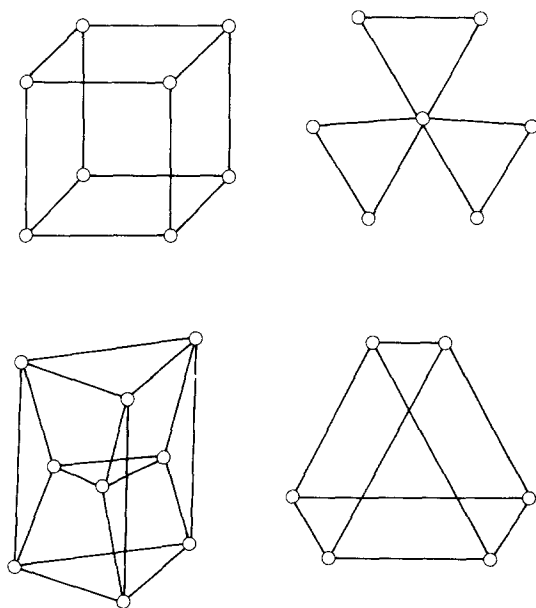Fig. 4. A more symmetrical representation of the graph of Fig. 3

Fig. 5. Several more symmetrical sub-graphs of the graph representing digonal twist mode (graph of Fig. 3)

Table 1. Adjacency matrix for the subgraph $G - K_5$

	AB	AC	AD	AE	BC	BD	BE	CD	CE	DE
AB	0	1	1	1	1	1	1	0	0	0
AC	1	0	1	1	1	0	0	1	1	0
AD	1	1	0	1	0	1	0	1	0	1
AE	1	1	1	0	0	0	1	0	1	1
BC	1	1	0	0	0	1	1	1	1	0
BD	1	0	1	0	1	0	1	1	0	1
BE	1	0	0	1	1	1	0	0	1	1
CD	0	1	1	0	1	1	0	0	1	1
CE	0	1	0	1	1	0	1	1	0	1
DE	0	0	1	1	0	1	1	1	1	0

partition the graph into disjoint set of vertices). When K_5 is taken as one component of G, we obtain as the other component the subgraph shown in Fig. 6, for which we used the same rule of labeling vertices as in the case of $\bar{G}$. The adjacency matrix for the subgraph of Fig. 6 is shown in Table 1, the vertices have been listed in the *alphabetical* order. The adjacency matrix reveals an interesting connection with the Petersen graph, arising in the isomerization of trigonal bipyramidal complexes. If nondiagonal zeros in the adjacency matrix are replaced by ones, and ones are replaced by zeros, which is precisely the analytical equivalent to constructing the complement of a graph, we obtain the Petersen graph. Moreover, the derived form for the adjacency matrix of the Petersen graph is the form associated with the *canonical* numbering of vertices in the Petersen graph [19]. The rule for the canonical numbering to which we refer is the one based on the concept of the smallest binary code for a graph when its adjacency matrix is viewed as a single string of digits read from left to right and from top to bottom [20]. Hence, the subgraph of Fig. 6 is the complement of the Petersen graph (Fig. 7). Again we find that two apparently unrelated processes – isomerizations in
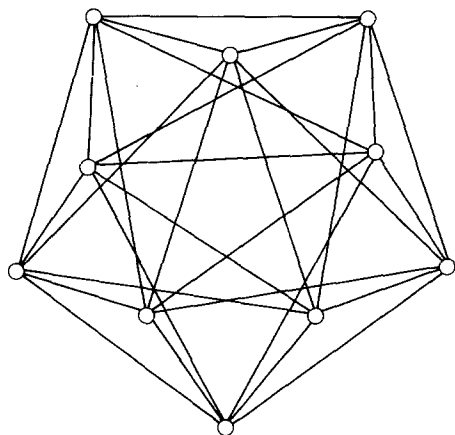
**Fig. 6.** One of the components of the graph of Fig. 3

octahedral complexes *via* digonal twist and an exchange of axial and equitorial roles for ligands in trigonal bipyramidal complexes – have a common mechanistic consequence. The processes are not equivalent; they happen to have related components.

The coincidence btweeen the *alphabetical* labels of the subgraph in Fig. 6 and the *canonical* labels of the Petersen graph, its complement, is remarkable and intriguing, and is clearly not accidental. It illustrates how the particular canonical labeling emerges naturally in some of the components of a graph. Alphabetical order is equivalent to a lexical ordering when letters are replaced by digits, so the interesting part of the coincidence consists in the relation between a lexical ordering of vertices, which have been labeled according to the rule of assigning double labels to $G - K_5$) component of a graph G, depending on the connectivity with K_5 component, and the canonical rule based on the smallest binary code for a graph. The coincidence shows a subtle relation of different labeling procedures, but because *both* labeling schemes are strictly *structural*, the coincidence reflects upon the innate structural features of the graphs and components considered. Because the complement of the subgraph of Fig. 6 is the Petersen graph with canonical labels representing the minimal binary code, the matrix of Table 1 corresponds to *maximal* binary code for the complement, i.e. the subgraph of Fig. 6. The alphabetical labels have some advantage too: observe that connected vertices *have no common labels.* For example, AB is connected to DE, CE, and CD. This is reminiscent of finding *outer* isomorphism in a graph having the symmetry S_6 [10]. In the search for outer isomorphism in S_6 one considers combination of two digits from six, so that connected vertices have no common digits. Here we use two out of five labels for one component of the graph and single labels for the other component. Thus, any permutation of the five labels in the component K_5 will induce permutation of its ten edges, which are characterized by a pair of labels and which lead to a 1:1 correspondence with the other subgraph. For example, the permutation (A, D, E, C)(B) induces a change of a double-letter label AB into BD and so on, and one obtains for the ten pairs the following permutation: (AB, BD, BE, BC)(AC, AD, DE, CE)(AE, CD). If one adopts the canonical numering of vertices, the above corresponds to the permutation: (1, 6, 7, 5)(2, 3, 10, 9)(4, 8), a symmetry element of the Petersen graph belonging to the class 2 4^2, discussed earlier in this series [19]. Hence, by finding that one can label the Petersen graph with two letter labels, so that adjacent vertices have no common letters, we can deduce that the Petersen graph has the same symmetry as K_5, the symmetry S_5, and the result was obtained *without* use of canonical labels.

4. Tetragonal-pyramidal complexes XY_4

For a given complex there are numerous distinctive isomerization modes involving different mechanisms, such as bond ruptures, rehybridization, charge migration, and change of geometry. Ruch and Haesselbarth [21], using double cosets, outlined a scheme for enumeration of different possible rearrangement modes in

various complexes. Klein and Cowley [22] considered a similar classification and labeling. Balasubramanian [23] in a series of papers considers formulation of methods to systematize and simplify associated group theory by using wreath product group, while Günthard and coworkers [24] developed the isometric group approach. For recent reviews on the subject consult an article by Ruch and Klein [25] on double cosets in chemistry and physics and book by Ezra [26] on symmetry properties of molecules where a more extensive bibliography on the subject can be found. In the case of pentacoordinated tetragonal-pyramidal complex, as
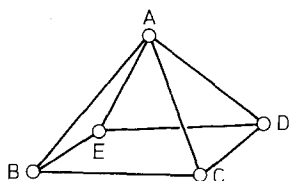
discussed by Balaban [27], there are seven distinctive rearrangement modes of chemical interest. The mode in which the apex ligand ligand A is exchanged with one of the four basal ligands B, C, D, or E, has already been examined within this series: first when enatiomers were ignored, and more recently with differentiation of enatiomers [28]. In both cases, the resulting graph has the valency $d = 4$, and the number of vertices is 15 and 30 respectively. The graphs have been found to have symmetries S_5 and $S_5 \times C_i$ with 120 and 240 permutation respectively. In addition there are modes of rearrangement of tetragonal-pyramidal complexes XY_4 which lead to complex graphs, and are represented by permutation of ligands as (BCA) or (AD)(BC), which are modes 6 and 7 in the paper of Balaban [27]. If one again neglects the difference between the corresponding enatiomers, the corresponding graph, as pointed out by Balaban, is the same for both modes. The graph is shown in Fig. 8, as depicted by Balaban. It has 15 vertices, all of degree 8. If one would consider enatiomers separately the resulting graph would have 30 vertices, and the two graphs for the two modes would be different [27], i.e. nonisomorphic. The graph of Fig. 8 and the graph of Fig. 2, the complement $\bar{G}$, both have 15 vertices, each of degree 8, so that one wonders if they are somehow related, even though one is associated with a rearrangement of a pentacoordinated tetragonal bipyramid and the other is associated (as a complement) with a rearrangement of octahedral complexes. The two diagrams do not overlap one another, so if the two graphs are isomorphic, the isomorphism has to be demonstrated. The graphs are sufficiently complex to suggest a use of a quick short-cut approach, e.g. an examination of selected invariants or subgraphs. Instead of considering canonical labels, which in this case are not easy to find, or trying the recently reported general scheme based on construction of the collection of characteristic equations [29], which are subsequently used in isomorphism tests (an application which requires use of a computer, in view of the size of the graph considered), we will show how one can demonstrate the isomorphism of the graphs of Fig. 2 and Fig. 8 in a few steps by recognizing useful subgraphs. Inspection of the graph of Fig. 8 again leads to K_5 as its *clique*
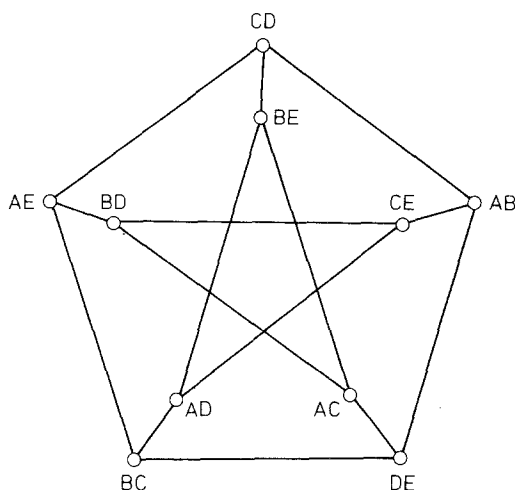
Fig. 7. The Petersen graph labeled so as
to match the labels of its complement
shown in Fig. 6

[2] (i.e. its maximal *complete* subgraph). When one assigns labels A, B, C, D, E
to the vertices of a K_5 subgraph, one can proceed applying the two-letter labeling
rule, and complete labeling of the graph. The process is unique, once vertices of
a selected K_5 clique have been labeled. Upon completion one can construct the
list of neighbors or write down the adjacency matrix and find that the result is
the same as for the graph of Fig. 2. This completes the proof that the two graphs
are isomorphic. This illustrates how, even without the use of canonical labels,
isomorphism of rather complex graphs can be established. Consequently, chemi-
cally different structures, tetragonal-pyramidal and octahedral complexes for
selected rearrangement modes, become mathematically equivalent.

Can we determine the order of the automorphism group without resorting to use
of canonical labels? Once we find K_5 as a clique and show that double-letter
labels can be assigned to the remaining ten vertices, we know that S_5 is a subgroup
of the sought symmetry group. If there is only one K_5 subgraph one would
conclude that the group of the larger graphs is also S_5, but in our case there is
more than one way of selecting a subgraph K_5. Hence, we need to find all possible
K_5 subgraphs, the task which need not be easy to perform. In our case, however,
one can be quickly convinced that there are, in all, six K_5 subgraphs: that is, five
in addition to the subgraph labeled ABCDE. To see this, consider the vertex A
and its connections: vertices AB, AC, AD, and AE. Together with A they form
another K_5 subgraph. Because in our graph all vertices are equivalent (this has
to be so if vertices are to represent equivalent isomers!) what is true for vertex
A will be true for B, C, D, and E. Formally we can recognize equivalence of all
K_5 subgraphs by using initially double (same) labels even for the K_5 component,
i.e. using AA, BB, CC, DD, and EE, instead of A, B, C, D, and E, respectively.
Then the remaining five K_5 subgraphs can be identified by erasure of a single
same label. If we erase A in AB, AC, AD, AE, and AA we obtain A, B, C, D, E,
which makes another relabeling of vertices possible, showing equivalence of all
six K_5 subgraphs. Because we have six K_5 graphs, each having 5! permutations,

there are in all 6! permutations for the composite graph and the symmetry is S_6, of order 720.

5. On the canonical numbering

If one desires to see individual permutations, how they exchange vertices, and which subgraphs are invariant under which operation, one has to list representative elements of the group for each class. In order to do this, *some* numbering of vertices has to be adopted. One can paraphrase George Orwell [30] by saying: "All numberings are arbitrary, but some are more arbitrary than others". Numbering that is based on some *structural* rule (as the two numberings mentioned in this work) is likely to be more useful in comparisons, ordering of graphs [31], fragment search, recognition of subgraphs, etc. Choosing a numbering for a structure is mathematically equivalent to selecting a coordinate system for a problem, and hence, as such does not enter the solution but can expedite solving the problem. In previous papers of this series [19, 28, 32] advantages of the canonical labels based on the smallest binary code for a graph have been illustrated. More recently the concept of the smallest binary code has been extended to cover unique coding of chemical reactions [33]. While we continue with the use of the smallest binary code, one should point to the fact that other *canonical* labelings are possible [34]. In particular, the recently discussed unique numbering and cataloguing of molecular structures by Hendrickson and Toczko [35] based on the *maximal* binary code is closely related, and is likely to be found computationally more similar than it may appear at first [36]. Search for canonical labels in general, is not an easy task, whether one uses minimal, maximal or some other rule for construction of the codes, because of the inherent $n!$ character of the problem of labeling of vertices. In the case of the graph of Fig. 8, the search for the minimal code labels can be facilitated by taking notice that the graph has subgraphs K_5 and also that all vertices are equivalent. In Fig. 9 we illustrated the initial steps in the search for the canonical labels. The position for label 1 was selected arbitrarily, and one of its nearest neighbors has been labeled as 15. Because all the vertices are eqivalent and there are four nearest neighbors, the selection of the sites for the labels 1 and 15 represents one out of $15 \times 8 = 120$ possibilities. Because, as mentioned previously, each vertex is common to two K_5 subgraphs, placing label 15 removes equivalence of the two subgraphs. Hence, without further analysis one cannot assign position for label 14. At this point the search branches into exploration of assignments that follow by placing label 14 within the same K_5 subgraph with vertices 1 and 15, and within the other K_5 subgraph having no vertex 15. Let's first outline the continuation of the search for the smallest binary labels by assuming that label 14 is assigned to the other K_5 subgraph of the vertex 1. Similar analysis and similar arguments would hold if we decided first to explore the possibilities of having label 14 assigned to a vertex of K_5 subgraph which already has label 15. The site for label 14 within the other K_5 is predetermined so to form the triangle 1, 14, 15. In order to by-pass a long list of possibilities derived from permuting the remaining labels 13–9 among the other vertices adjacent to vertex 1, we use a single unspecified label
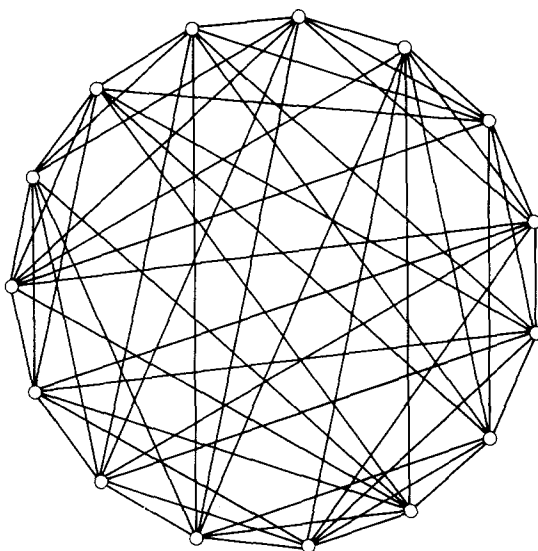
Fig. 8. Graph representing an isomerization of tetragonal-pyramidal complexes as given by Balaban [27]

a but restricting *a* to values 13, 12, 11, 10, 9, and 8. Label 2 is placed adjacent to *both* 15 and 14. In fact, this dictated the site of 14 as part of the 1, 14, 15 triangle, because other possibilities would not produce at vertex 2 optimal neighbors: 14, 15. All the neighbors of vertex 2 are labeled at this stage as *b*, with *b* = 7, 6, 5, 4. The only site *without* a label is now labeled as 3. Observe that label 2 has three possible sites (there are three triangles with the side 15, 14), which brings the total number of possibilities so far to 120 × 3 = 360. In the continuation of the assignment one finds that label 4 has two alternative sites, giving for the order of the group 360 × 2 = 720. All not yet specified positions have unique labels and these are (because they are unique!) not difficult to find. First locate those *a* sites that are adjacent to label 2 (there are two such sites) and give them the largest labels in set *a*: 13/12. The slash notation signifies that 13 and 12 are used as pair labels, but we have not yet decided which vertex receives label 13 and which receives label 12. With the selection of the site for label 4 one assigns labels 11/10 to *a* vertices adjacent to vertex 4 and consequently deduces for the remaining nonadjacent sites of vertex 4 having label *a* labels 9/8. At the same time one can assign labels 7/6 to *b* vertices adjacent to 4, the highest available labels restricted to *b*. This prescribes 5 for the remaining *b* vertex label. An inspection of the neighbors for the two 7/6 sites shows that they are not equivalent, i.e. one will result in a smaller binary code than the other. The neighbors for one of the two sites are (2, 3, 4, 5, 10, 11, 12, 13) even though we do not know definitive places for several labels in the list of neighbors. The other site has neighbors (2, 3, 4, 5, 8, 9, 14, 15) and clearly corresponds to a larger binary code, because after an identical initial list it would give as neighbor to vertex 6 vertices with label 8 and 9 rather than 10 and 11 available in the first alternative. In a similar manner one can select between two 9/8 sites and find that label 8 has, as neighbors, 13 and 11 from the undecided pairs 13/12 and 11/10. In Fig. 10 we give the final

Table 2. Adjacency matrix for the graph G with the canonical numbering of vertices

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1
2	0	0	0	1	1	1	1	0	0	0	0	1	1	1	1
3	0	0	0	1	1	1	1	1	1	1	1	0	0	0	0
4	0	1	1	0	0	1	1	0	0	1	1	0	0	1	1
5	0	1	1	0	0	1	1	1	1	0	0	1	1	0	0
6	0	1	1	1	1	0	0	0	0	1	1	1	1	0	0
7	0	1	1	1	1	0	0	1	1	0	0	0	0	1	1
8	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1
9	1	0	1	0	1	0	1	1	0	1	0	1	0	1	0
10	1	0	1	1	0	1	0	0	1	0	1	1	0	1	0
11	1	0	1	1	0	1	0	1	0	1	0	0	1	0	1
12	1	1	0	0	1	1	0	0	1	1	0	0	1	1	0
13	1	1	0	0	1	1	0	1	0	0	1	1	0	0	1
14	1	1	0	1	0	0	1	0	1	1	0	1	0	0	1
15	1	1	0	1	0	0	1	1	0	0	1	0	1	1	0

result and the adjacency matrix is shown in Table 2. Were we pursuing the alternative assignment of label 14 we would end with labels that would correspond to binary code which is greater than one here found.

Representative permutations, each belonging to a different class, are listed in Table 3. These representative permutations can be found using known elements for the complement graph and seeking the correspondence between the labels in the two graphs, rather than using the canonical labels for many copies of the graph (all being canonical) and comparing different labels. An examination of the adjacency matrix of the graph of Fig. 8 allows one to find the correspondence of labels relatively quickly. One first replaces off-diagonal zeros by 1's and searches for those rows that have a common entry in one of the columns. For the graph of Fig. 8 we find that rows 1 and 2 have a common zero (or 1 if zeros have been

Table 3. Representative permutations (one of each of the 11 classes of S_6)

(1)(2)(3)(4)(5)(6)(7)(8)(9)(10)(11)(12)(13)(14)(15)	1^{15}
(1)(2)(3)(4)(5)(6)(7)(8, 9)(10, 11)(12, 13)(14, 15)	$1^7\,2^3$
(1)(2)(3)(4, 6)(5, 7)(8, 9)(10, 11)(12, 15)(13, 14)	$1^3\,2^6$
(1)(2, 6, 4)(3, 5, 7)(8)(9)(10, 12, 14)(11, 13, 15)	$1^3\,3^4$
(1)(2, 6, 4)(3, 5, 7)(8, 9)(10, 13, 14, 11, 12, 15)	$1\,3^2\,2\,6$
(1)(2)(3)(4, 5)(6, 7)(8, 10)(9, 11)(12, 15)(13, 14)	$1^3\,2^6$
(1)(2, 4, 3, 5)(6, 7)(8, 12, 15, 10)(9, 13, 14, 11)	$1\,2\,4^3$
(1)(2, 4, 3, 5)(6, 7)(8, 13, 15, 11)(9, 12, 14, 10)	$1\,2\,4^3$
(1, 3, 2)(4, 12, 11, 5, 15, 9)(6, 13, 8, 7, 14, 10)	$3\,6^2$
(1, 3, 2)(4, 13, 9)(5, 14, 11)(6, 12, 10)(7, 15, 8)	3^5
(1, 5, 15, 9, 2)(3, 4, 10, 6, 11)(7, 14, 12, 13, 8)	5^3
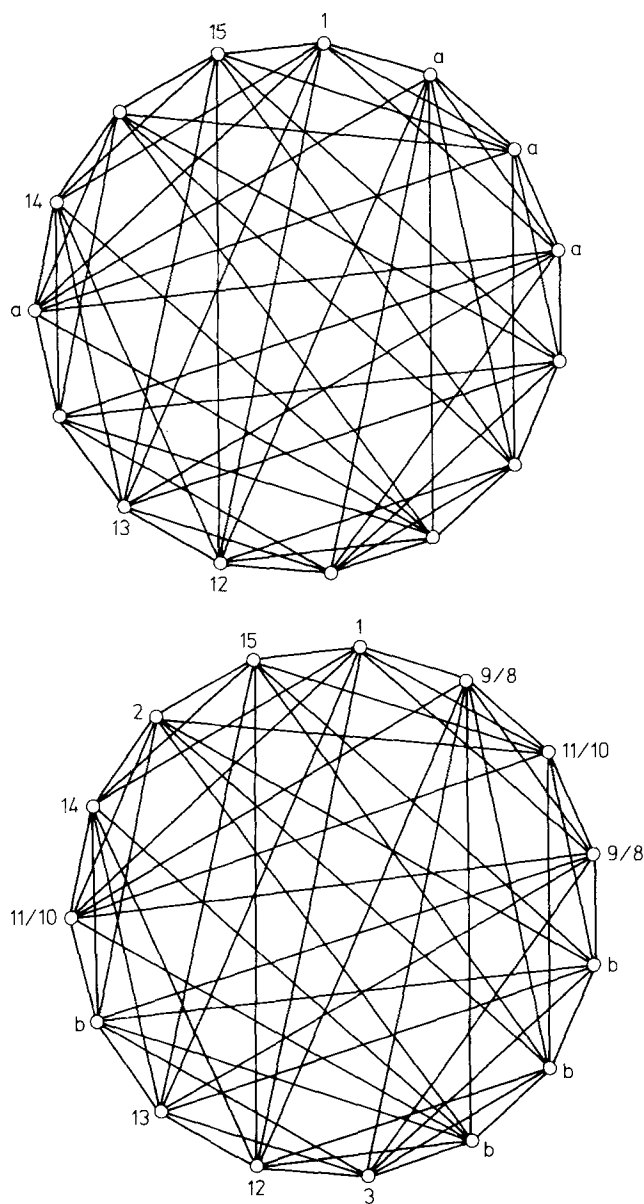
Fig. 9. The initial steps in the search for the canonical labels of the graph representing isomerization of XY_4 complexes

replaced) in column 3; therefore, 1, 2, 3 make a triangle. Similarly, 1, 4, 5 and 1, 6, 7 make triangles. The remaining labels are then easy to locate. The correspondence between the labels of the graph of Fig. 2 and the graph of Fig. 8 is then:

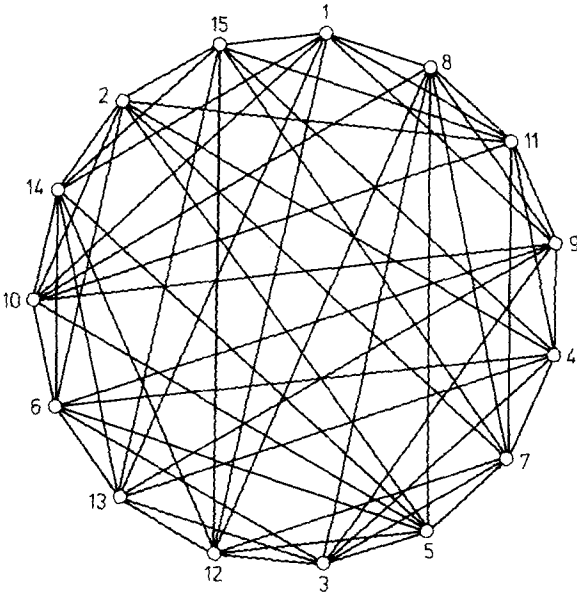| Fig. 2:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Fig. 8:	1	15	10	14	11	13	12	2	6	7	3	8	4	9	5

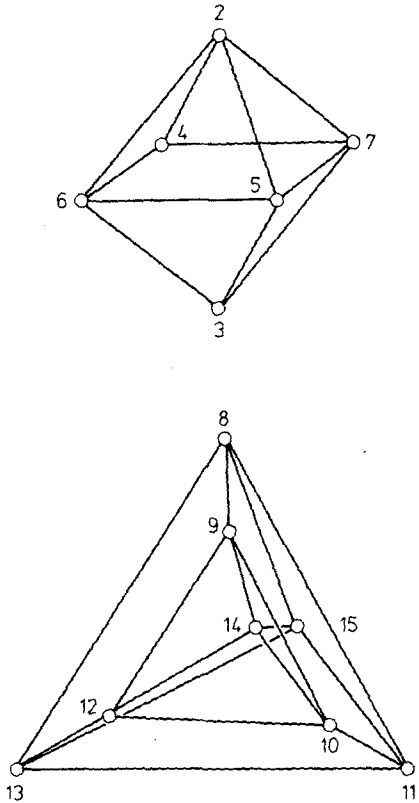**Fig. 10.** The canonical labels for the graph considered

Fig. 11. Highly symmetrical subgraphs of the graph of Fig. 8 discerned from the canonical labelings and associated adjacency matrix (Table 2)

With the above correspondence, one can "translate" an element of symmetry of one graph into the corresponding element for the other.

Finally let's point to some additional properties of the canonical labeling of the graph in Fig. 8. Consider the submatrix involving rows and columns 2–7. The corresponding subgraph is shown in Fig. 11. When vertices are relabeled by using labels from 1–6, by decreasing each label value by one, the canonical labeling for the subgraph results. The rows and columns 8–16 define another subgraph, a highly symmetrical "tetrahedron-in-tetrahedron" (simplex polycorypha bounded by two tetrahedra and four pentahedra). This is one of the two types of simplex polycoryphas with six cells. The other has been shown in Fig. 5.

6. Concluding remarks

Graphical representation of the relations among isomers in various rearrangement modes has an advantage of mathematical abstraction and consequently different chemical systems and structures can be found to have an equivalent mathematical description. In addition, possibilities of different pictorial representation may make different aspects of a same problem more visible. While difficulties associated with high symmetry of the problem of recognition of graphs are present, they can be resolved in a systematic way by use of canonical labels or alternative schemes for differentiating otherwise equivalent vertices. Finally, as discussed in this paper, even information on fragments, components and subgraphs can relate different graphs (i.e. different chemical transformations) or find some common feature in otherwise distinctive problems. Use of complementarity is one of the illustrations of a unified character in many processes. It not only helps to solve and recognize such cases but reflects the underlying reciprocity between a chemical phenomenon and a mathematical ideal.

7. Appendix

Glossary of graph theoretical terms

Adjacency matrix: A matrix, the rows and columns of which correspond to the vertices of a graph and the elements of which are either ones or zeros depending on whether the corresponding vertices are linked or not respectively.
Complementary graph: Graph $\bar{G}$ obtained by deleting the edges of a given graph G from a complete graph K_n having the same number of vertices.
Complete graph K_n: Graph having n vertices in which every pair of vertices is connected.
Degree of a vertex d: The number of edges with which the vertex is incident.
Graph: (informally) mathematical object consisting of points (called vertices) and connections (called edges) linking some of these vertices. (formally): A mathematical system consisting of two sets V and E, together with a mapping G of E into $V \times V$ (Descartes product, the set of unordered pairs of elements of V).

Isomorphic graphs: A pair of graphs whose vertices and edges can be placed in 1–1 correspondence so that the adjacency relations (list of neighbors) are preserved.

Regular graph: A graph in which all vertices are of a same degree.

Automorphism: A one-one mapping S of the vertex set of G onto itself with the property that $S(v_i)$ and $S(v_j)$ are adjacent if and only if v_i and v_j are.

Clique: A maximal complete subgraph.

Component of G: (as used here) A subset of vertices and all mutually connecting edges. This definition, as special case applies to disconnected subgraphs (fragments).

Hamiltonian circuit: A closed path which passes exactly once through each vertex.

Line Graph L(G): The graph whose vertices are in one-one correspondence with edges of G, two vertices of $L(G)$ being adjacent if and only if the corresponding edges of G are adjacent.

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