

GRAPHS CORRESPONDING TO INTRAMOLECULAR REARRANGEMENTS

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In recent years several chemists have investigated rearrangements of the ligands in coordination complexes and have drawn graphs to depict their results. Most accounts of this work assume that the reader is familiar with chemical terminology and are, therefore, not easy for graph theorists to read. The present paper, aimed at both graph theorists and chemists, starts with some chemical background, then discusses the graphs which arise with five and six coordination and concludes by taking a brief look at the problems involved in obtaining the graphs for higher coordination numbers.

2. Coordination complexes

There is an extensive class of chemical compounds collectively known as coordination complexes (or coordination compounds). They are defined [6] as "substances with characteristic chemical structures in which a central metal atom is surrounded by chemical bonds". The number of ligands in a complex is called the coordination number and a general complex with n ligands is often denoted by ML_n . The geometrical arrangement of the ligands is the coordination geometry, and a complex may be represented by drawing the appropriate polyhedron and labelling its vertices to correspond the ligands.

Uranium hexafluoride UF_6 is an example of an ML_6 complex with octahedral geometry. Fig. 1a indicates the bonding of the

fluorines to the uranium atom (the dotted lines indicating the plane in which five of the atoms lie); fig. 1b depicts a regular octahedron with its vertices labelled.

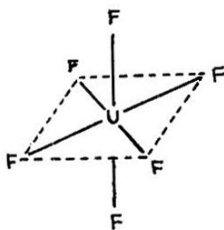


Fig.1a

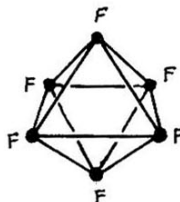


Fig.1b

Another example, also with octahedral geometry, is the dichloro-tetraammine-cobalt(III) ion where two of the ligands are chlorine atoms and the other four are ammonia molecules. In this case there are two forms of the complex (fig. 2/3) called the cis and trans forms. These two forms are examples of stereoisomers - molecules having identical components but which differ in their relative spatial orientation in the molecule (see, for example, Rouvray [11]).

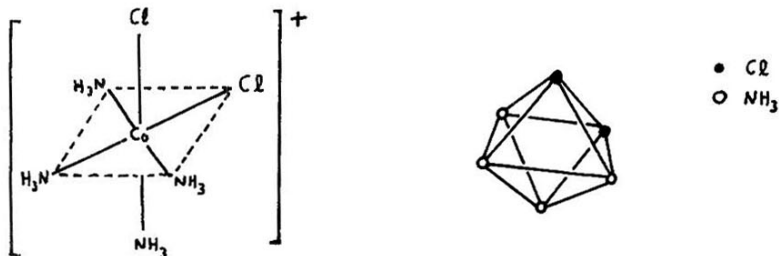


Fig.2 Cis form of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.

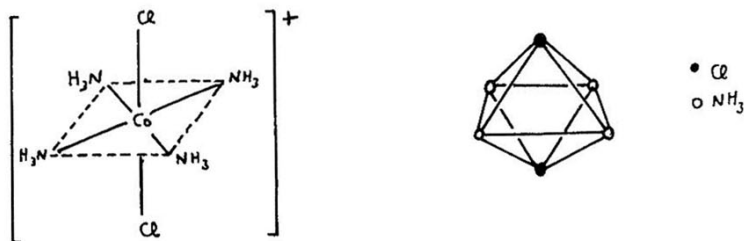


Fig.3 Trans form of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.

In mathematical terms counting stereoisomers of a coordination complex with specified geometry is equivalent to counting the number of different ways of labelling the vertices of the corresponding polyhedron. If all n ligands are different from one another then the number is just $n!/r$ where r is the order of the rotation group of the polyhedron. If two different isomers are simply mirror images of one another, then they are called enantiomers and for some purposes are regarded as being equivalent, in which case the number of isomers is $n!/2r$, since the full symmetry group of the polyhedron (including the reflections) has order $2r$. If not all the ligands are different then the Redfield-Pólya theorem [2 chap.4, 8, 10] provides a systematic method for calculating the number of isomers with given geometry.

3. Isomerisations of ML_5

Various chemical mechanisms are known which convert one stereoisomer of a coordination complex into another and several authors [1, 3, 4, 5] have constructed graphs as a means of showing which isomerisations are possible under the action of a given mechanism. This will be illustrated by examining ML_5 with trigonal bipyramidal geometry and all ligands different. Fig.4a depicts such a molecule (where the dotted line leads to an atom behind the plane of the paper and the wedge shaped line to an atom in front of the plane); fig. 4b the corresponding polyhedron. Vertices 1 and 2 are called axial; 3, 4, 5 equatorial.

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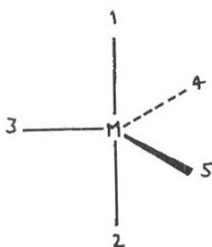


Fig. 4a

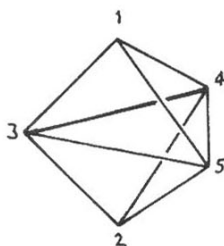


Fig. 4b

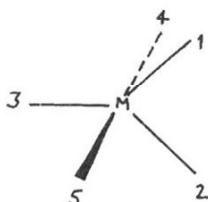


Fig. 5a

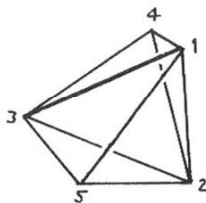


Fig. 5b

In the Berry mechanism (or pseudorotation), one of the equatorial ligands retains its position but the other ligands are rearranges. Ligands 1, 2, 3 remain coplanar but the angles $3M1$ and $3M2$ increase from 90° to 120° whilst at the same time 3, 4, 5 remain coplanar but the angles $3M4$ and $3M5$ decreases from 120° to 90° . There is an intermediate position in which the geometry is that of the square pyramid but the end result is again a trigonal bipyramid but with 4 and 5 as axial ligands (fig. 5). Altogether there are twenty possible isomers and fig. 6 depicts a graph in which the vertices correspond to the isomers and in which two vertices are joined if and only if the corresponding isomers can be interconverted by applying a single Berry mechanism.

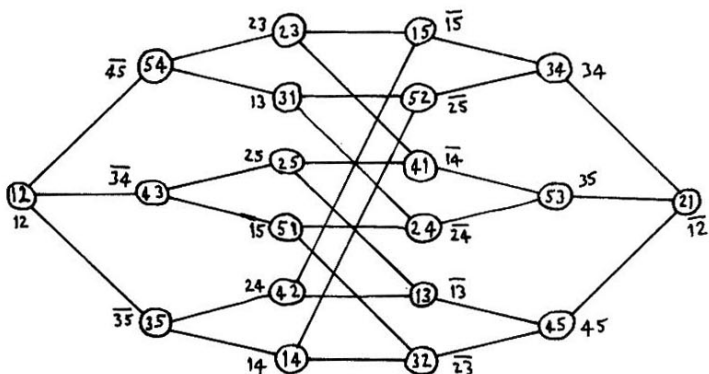


Fig.6 Desargues-Levi graph, showing two different notations for the vertices (see [9] for alternative drawings).

Various notations have been used for the isomers, two of which are given in fig. 6. The notation placed on the vertices consists of a pair of digits, such as 53. The corresponding isomer is the one in which 5 and 3 are axial ligands and in which the remaining ligands 1, 2, 4 are arranged clockwise in increasing numerical order when viewed from ligand 5 (fig. 7).

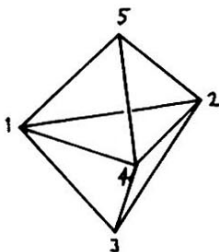


Fig.7 Isomer 53.

This notation has the disadvantage that it does not provide a simple rule for constructing the graph. In the alternative notation (shown alongside the vertices in fig. 6) the labels consist of a pair of unordered digits, half of the pairs being barred. Now the rule for constructing the graph is simple: two vertices are joined if and only if (1) their labelling sets are disjoint and (2) precisely one vertex of the pair is barred. Thus 12 is joined to $\overline{34}$ but 23 is not joined to $\overline{25}$ since the symbol 2 is common to the latter pair of vertices. The disadvantage of the alternative notation is that whilst ab and \overline{ab} are the two enantiomers with a and b as axial ligands it is not possible to give a simple rule explaining which enantiomer is which. (Gielen [5] uses a similar notation but his choices for barred elements is slightly different from that in fig. 6) The graph is well-known to graph theorists and is called the Desargues-Levi graph since it is connected with the beautiful theorem of Desargues in projective geometry.

If enantiomers are identified then the twenty isomers reduce to ten and the corresponding graph is that obtained by identifying vertices ab and \overline{ab} for all a and b . The result (fig. 8) is Petersen's graph [7], known since 1898.

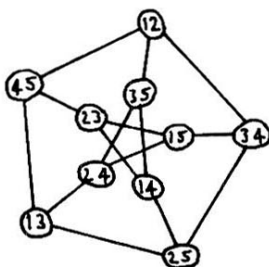


Fig. 8 Petersen's graph.

If the permutation (1425) is applied to isomer 12 (fig. 4) then the result is again isomer 54 (fig. 5). Hence there is a connection between permutations and mechanisms, which is examined in detail by Dugundji, Gillespie, Marquarding, Ugi and Ramirez [4]. They also look at other mechanisms (as does Gielen [5]) and at cases where not all ligands are different. Other mechanisms turn out to be equivalent to applying a sequence of Berry mechanisms. The graph corresponding to a sequence of n Berry mechanisms ($1 \leq n \leq 5$) will be denoted by $D^{(n)}$. It has the same vertex set as the Desargues-Levi graph $D^{(1)}$ and two vertices are joined in $D^{(n)}$ if and only if they are distance n apart in $D^{(1)}$. [The distance between two vertices in a graph is the length of (number of edges in) a shortest path joining the vertices.] The graphs $D^{(2)}$ to $D^{(5)}$ are illustrated in fig. 9 to fig. 12, where the notations and names for the mechanisms follow Gielen [5].

If some ligands are equivalent then the corresponding graphs are obtained by identifying appropriate vertices in $D^{(1)}$ to $D^{(5)}$ (see [4] for examples). A further variation of the problem is considered by Clark and Kettle [3] in which one ligand, e.g. 5, always remains equatorial. Deleting vertices which include the number 5 from Petersen's graph (fig. 8) gives the graph of fig. 13; its complement (the octahedral graph) is shown in fig. 14. These are the two graphs obtained by Clark and Kettle.

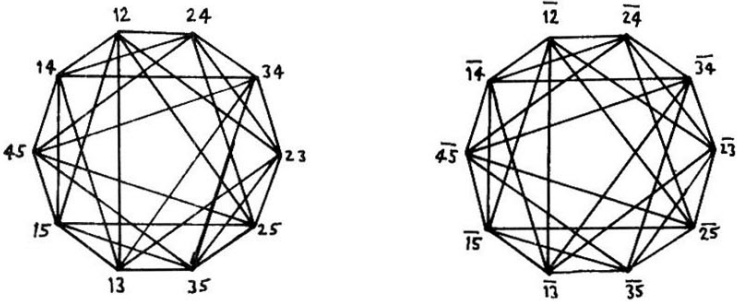


Fig. 9 The graph $D^{(2)}$ of the mechanism P2. Alternative drawings appear in [4, p 151] and [5, p 276]. Each component is the complement of Petersen's graph (i.g. two vertices are joined if and only if they are not joined in Petersen's graph).

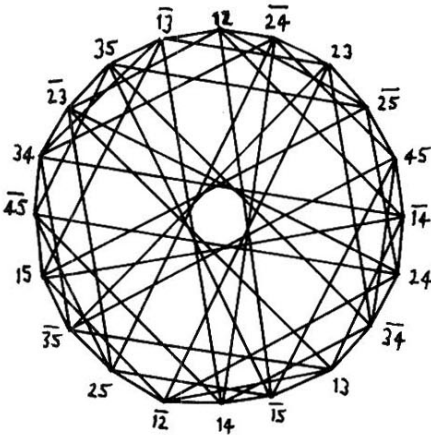


Fig. 10 The graph $D^{(3)}$ of mechanism P3. The graph contains a pair of edge disjoint Hamiltonian circuits, each using alternate edges of the Hamiltonian circuit displayed here:

12- $\overline{24}$ -14- $\overline{12}$ -13- $\overline{15}$ -35- $\overline{13}$ -34- $\overline{23}$ -24- $\overline{34}$ -45- $\overline{14}$ -15- $\overline{45}$ -25- $\overline{35}$ -23- $\overline{25}$ -

and

12- $\overline{13}$ -23- $\overline{24}$ -45- $\overline{25}$ -24- $\overline{14}$ -13- $\overline{34}$ -14- $\overline{15}$ -25- $\overline{12}$ -15- $\overline{35}$ -34- $\overline{45}$ -35- $\overline{23}$ -

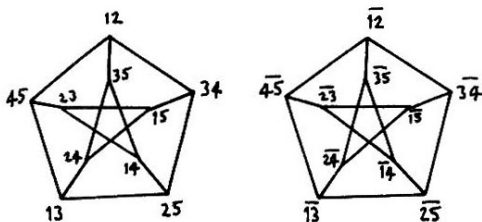


Fig. 11 The graph $D^{(4)}$ of the Hamiltonian circuit mechanism P4. Each component is a Petersen graph, but although P4 corresponds to a Hamiltonian circuit in the trigonal bipyramid Petersen's graph does not contain a Hamiltonian circuit!

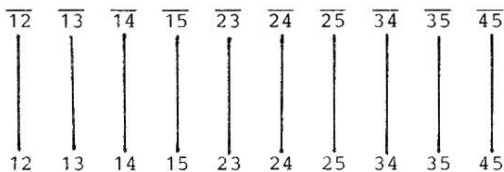


Fig. 12 The graph $D^{(5)}$ of the digonal twist mechanism P5.



Fig. 13 Graph of Berry mechanism (disregarding enantiomerism) with ligand 5 always equatorial.

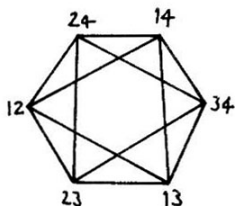


Fig. 14 The octahedral graph.

4. Isomerisations of ML_6

For six coordination octahedral geometry is most common and the corresponding graphs for various mechanisms have been discussed by Balaban [1]. If all ligands are different then there are thirty isomers, or fifteen disregarding enantiomerism. The graph for the digonal twist mechanism (i.e. the interchange of a pair of adjacent vertices of the octahedron) appears in fig. 15 in one of the ways that Balaban draws it but with a different notation for the isomers. Here each vertex is labelled with an unordered pair of numbers from 1, 2, 3, 4, 5, 6 and two vertices are joined if their labelling sets are disjoint. This notation does not give a simple rule for determining the corresponding isomers and is rejected by Balaban who uses a less symmetrical two digit notation. Yet another notation for the isomers is to specify the three pairs of labels on opposite vertices of the octahedron (fig. 16).

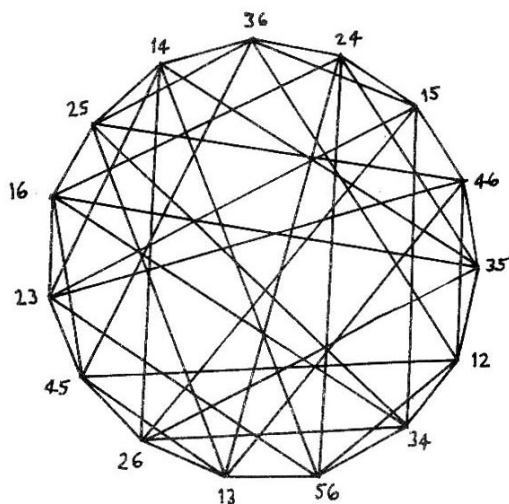


Fig.15

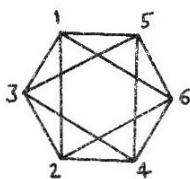


Fig.16 Isomer (14)(25)(36).

A possible correspondence between the notations of fig. 15 and fig. 16 is given in table 1. The correspondence is connected with the fact that S_6 is the only symmetric group which has outer automorphisms and those automorphisms interchange permutations of type (ab) with those of type (uv)(wx)(yz). An alternative notation often throws additional light on a subject and by

using the notation of fig. 15 the author discovered a Hamiltonian circuit in the graph with five-fold symmetry (fig. 17). Another way to visualise this interesting graph is indicated in fig. 18. The vertices distance two from 12 form a cube. Vertex

(12) (34) (56) (36)	(13) (26) (45) (46)	(15) (24) (36) (34)
(12) (35) (46) (45)	(14) (23) (56) (14)	(15) (26) (34) (15)
(12) (36) (45) (12)	(14) (25) (36) (56)	(16) (23) (45) (35)
(13) (24) (56) (25)	(14) (26) (35) (23)	(16) (24) (35) (16)
(13) (25) (46) (13)	(15) (23) (46) (26)	(16) (25) (34) (24)

34 is joined to the four vertices lying on an opposite pair of edges in the cube; 56 to the remaining vertices in the cube. Similarly 35, 46 and 45,36 are joined to other choices of vertices lying on opposite edges.

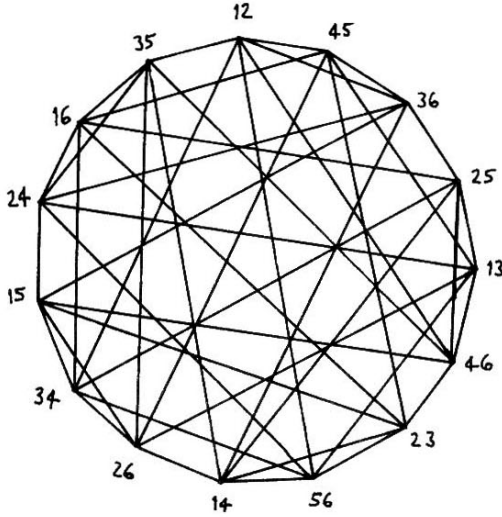


Fig. 17 The two-symbols-from-six graph is an edge-disjoint union of three Hamiltonian circuits: the one in the figure, together with 12-36-14-23-15-26-13-45-16-25-34-56-24-35-46- and 12-56-13-36-15-46-25-14-35-26-45-23-16-34-.

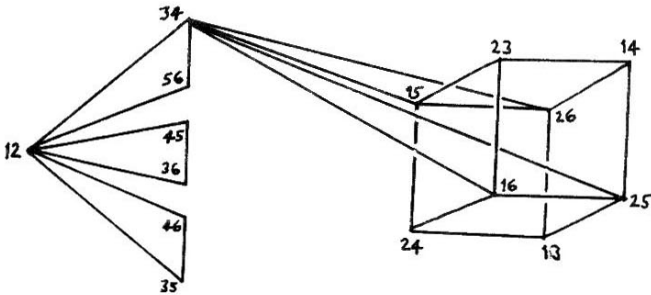


Fig. 18 Another realisation of the graph - some edges are omitted for clarity.

5. Higher coordination numbers

With coordination numbers greater than six the number of isomers is excessively large if all the ligands are different. Consequently in order to obtain insight into that case it will be necessary to examine first cases in which some of the ligands are identical. Unfortunately such cases lead to less symmetrical graphs than for all ligands different.

To the chemist the dodecahedron is the polyhedron in fig. 19; to the mathematician that in fig. 20 (both have twelve faces and so both are indeed dodecahedra!). There are fifteen isomers of ML_8 with dodecahedral geometry when four ligands are of type X and four of type Y. One of them is shown in fig. 21a. The subgraph consisting of the vertices of type X and the edges joining them is shown in fig. 21b. It is convenient to denote the isomers by the subgraphs and all fifteen are listed in table 2. Interchange of a pair of adjacent vertices of the polyhedron leads to the graph in fig. 22 which has a symmetry group of order two.

Acknowledgements

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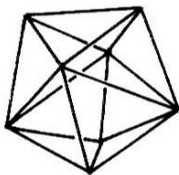


Fig.19 Trigonal dodecahedron.

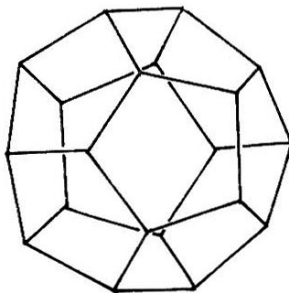


Fig.20 Pentagonal dodecahedron.

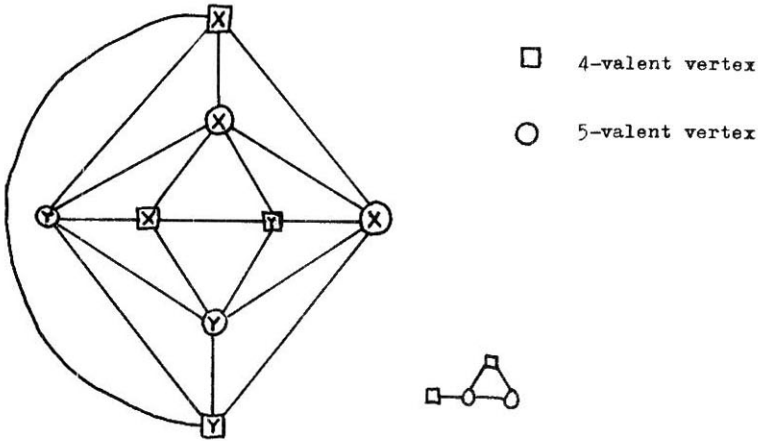


Fig. 2.1a Isomer 11.

Fig. 2.1b Subgraph of X vertices.

Table 2; Isomers of MX_4Y_4			
1	2	3	4
5	6	7	
8	9	10	11
12	13	14	15

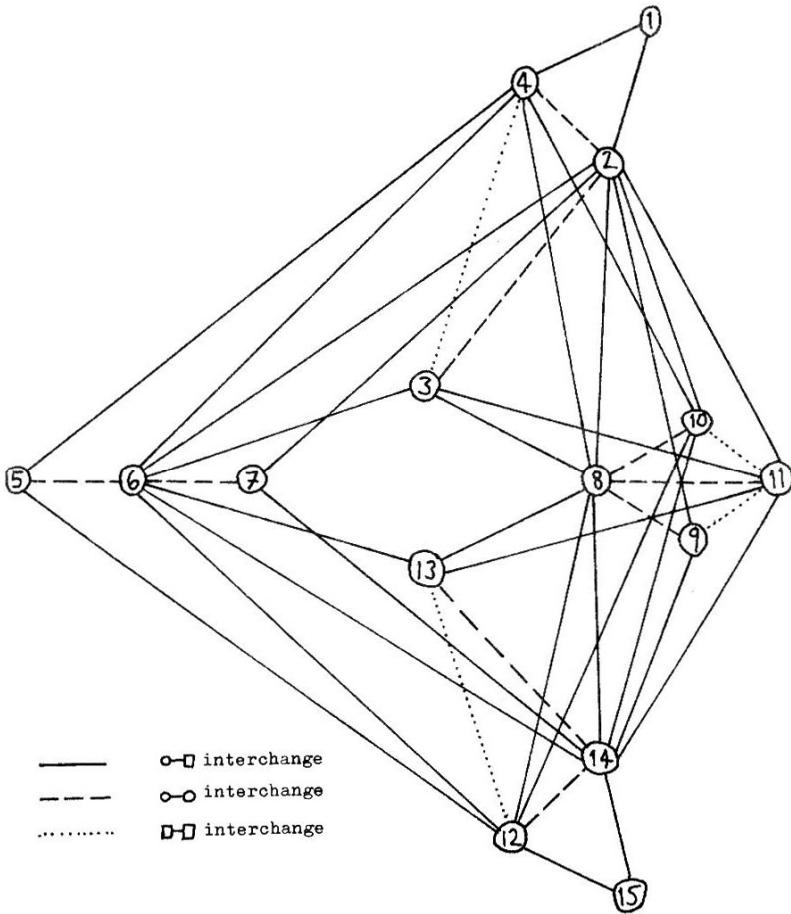


Fig.22 Graph of MX_4Y_4 with dodecahedral geometry.

References

[Extensive references are given by Balaban, Dugundji et al, and Gielen]

- 1(a) Balaban, A.T., Fărcașiu, D. and Bănică, R., Chemical Graphs II. Graphs of multiple 1,2-shifts in carbonium ions and related systems. Rev. Roumaine Chim. 11 (1966), 1205-1227.
- (b) Balaban, A.T., Chemical graphs XVI. Intramolecular isomerizations of octahedral complexes with six different ligands. Rev. Roumaine Chim. 18 (1973), 841-854.
- (c) Balaban, A.T., Chemical graphs XIX. Intramolecular isomerizations of trigonal bipyramidal structures with five different ligands. Rev. Roumaine Chim. 18 (1973), 855-862.
2. Biggs, N.L., Lloyd, E.K., and Wilson, R.J. Graph theory 1736-1936. Clarendon Press, Oxford, 1976.
3. Clark, M.J. and Kettle, S.F.A., Incidence and distance matrices. Inorg. Chim. Acta 14 (1975), 201-205.
4. Dugundji, J., Gillespie, P., Marquarding, D., Ugi, I. and Ramirez, F., Matric spaces and graphs representing the logical structure of chemistry. In: Chemical applications of graph theory (ed. A.T. Balaban), Academic Press, London, 1976
5. Gielen, M., Applications of graph theory to organometallic chemistry. In: Chemical applications of graph theory (ed. A.T. Balaban), Academic Press, London, 1976.
6. Halpern, J., Coordination compounds. Enc. Britannica (15th edn.) 5 (1974), 134-143.
7. Petersen, J. [Sur le théorème de Tait.] Interméd. Math. 5 (1898), 225-227.
8. Pólya, G., Kombinatorische Anzahlbestimmungen für Gruppen, Graphen und chemische Verbindungen. Acta Math. 68 (1937), 145-254.
9. Randić, M., On discerning symmetry properties of graphs. Chem. Phys. Letters 42 (1976), 283-287.
10. Redfield, J.H., The theory of group-reduced distributions. Amer. J. Math. 49 (1927), 433-455.
11. Rouvray, D., The mathematical theory of isomerism. Chemistry 45 (Feb. 1972), 6-11.