PROBLEM OF THE CLASSIFICATION OF COORDINATION POLYHEDRA

P. I. Lazarev, M. A. Poraи-Koshits, and M. I. Lazarev

In connection with the sharp increase in the number of structural papers in the field of coordination compounds, the need for a single system for the description of the geometry of complexes is becoming increasingly apparent. It is obviously desirable that this system should make it possible to carry out quantitative estimates of the degree of distortion of the form of a complex, that is, to estimate the "distance" to some most characteristic and generally familiar geometric form. This problem was solved in [1] for eight-apex complexes. The proposed approach provides a quantitative model of the process by which the expert assigns a real eight-apex figure to one of the types of ideal eight-apex figures. It is assumed that the expert knows all types of possible polyhedra, and a comparison of the external geometric forms of the polyhedra is carried out. The criteria for the assignment of a polyhedron to a definite type, developed in this approach, have a number of unsatisfactory features: 1) the restriction to one value of the coordination number; 2) the need for an a priori knowledge of all possible types of polyhedra characteristic of the given coordination number; 3) the use, as standards, of ideal forms of polyhedra, and not the stereochemically most characteristic forms; and 4) the use of external forms of polyhedra which have no physical significance.

The present paper describes an attempt to construct a classification algorithm free from the above limitations. It is also assumed that we know the coordination number of the metal atom.

The problem of classifying any objects includes firstly the selection of a system of characteristics, within the framework of which the comparison of the objects will be carried out, and secondly the actual breakdown of the original set of objects into classes (subsets). Here our intuitive ideas regarding the best classification correspond to that classification in which the objects placed in the same class show the maximum "similarity," and the representative of different classes show the maximum differences.

CHOICE OF THE SYSTEM OF CHARACTERISTICS

The system of characteristics selected for the description of the objects being classified should provide a sufficiently complete description of the object and, where possible, should not contain excess information.

In carrying out the classification of the coordination polyhedra of a metal or a group of chemically similar metals, the stereochemical behavior of the complex-forming metal atom is of chief interest, whereas the nature of the ligand can often be neglected. The system of characteristics should therefore be related to the geometric characteristics of the metal atom. Moreover, the characteristics should have a clear physical significance. These two requirements are satisfied by the system of characteristics which we selected, namely, the set of all possible angles between the lines drawn from the central atom to the atoms situated at the apices of the coordination polyhedron.

The elements of the set have significance if they correspond to the angles between the directions of the metal-ligand bonds or (since we are interested in the nature of the ligand) between the orbitals of the complex-forming atom. Thus the proposed system of characteristics is sufficiently complete and is related to the stereochemical characteristics of the metal atom, and the characteristics have physical significance. The proposed sys-
tern of characteristics is sufficient for the classification of the geometric forms of complexes. If the purposes of the classification are extended, it is possible to supplement the system of characteristics by introducing the physical and chemical properties of the ligand molecules appearing in the complex, and also the properties of the crystals as a whole. The construction of a system of characteristics taking account of differences in the nature of the ligands is also undoubtedly possible.

CONSTRUCTION OF THE CLASSIFICATION ALGORITHM

We shall make use of the classification methods developed in the theory of pattern recognition [2-4]. We shall assume that we have \( m \) \( N \)-apex figures, given by sets of the angles between the lines drawn from the center to the apices. The aim of the classification is to break down the set of \( N \)-apex figures \( X = \{ x_k \} \) into subsets.

We introduce the distance between the elements of the set \( X \), ordering each set of angles in increasing order

\[
    r_{ij} = \left[ \sum_{k=1}^{p} (\alpha_{ik} - \alpha_{jk})^\kappa \right]^{1/\kappa}
\]

where \( \kappa \) is a given parameter, for example \( \kappa = 2 \).

We introduce the potential created at \( x_i \) by the point \( x_j \):

\[
    \varphi(x_i, x_j) = \left( a + b \frac{\alpha}{r_{ij}} \right)^{-1}
\]

where \( r_{ij} \) is the length of the vector \( r_{ij} \), and \( a, b, \) and \( \alpha \) are arbitrarily chosen parameters (for example, if \( a = b = 1 \) and \( \alpha = 2 \), it follows that \( \varphi \) is a potential of the Coulombic type for isolated charges).

We separate from the original set \( X = \{ x_i \}, i = 1, 2, \ldots, m \), a subset \( Y_1 = \{ x_i \}, i = 1, 2, \ldots, k \), and a subset \( Y_2 = \{ x_j \}, j = k + 1, 2, \ldots, k + p \). The average potential created by \( y_1 \) at the point \( x \neq y_1 \) is equal to

\[
    q(x, y_1) = \frac{1}{k} \sum_{i=1}^{k} \varphi(x, x_i), \text{ where } x_i \in Y_1,
\]

and the average potential created by \( y_1 \) at \( y_2 \) is equal to \( q(y_2, y_1) = \frac{1}{p} \sum_{j=1}^{p} \varphi(x_j, y_1) \), where \( x_j \in Y_2 \). We define the characteristic potential of the subset \( Y_1 \) as

\[
    \varphi(Y_1, y_1) = \frac{2}{k(k-1)} \sum_{i=1}^{k} \sum_{j=i+1}^{k} \varphi(x_i, x_j), \quad x_i, x_j \in Y_1.
\]

From the definition of \( \varphi(y_1, y_1) \) it can be seen that it provides a measure of the similarity of the points within the subset \( Y_1 \). We shall assume that we know the number of subsets \( q \) into which the original set \( X \) should be broken down. This means that we have to assign each \( x \) to one out of \( Y_1, Y_2, \ldots, Y_q \). We shall assume first of all that each element \( x_i \) is a subset \( (i = 1, 2, \ldots, m) \). We shall make use of a procedure in which, in each step, the two nearest subsets are combined into one. The step consists of the search for \( \max \varphi(y_1, y_2), j \neq i \) and the combination of the corresponding \( y_1 \) and \( y_2 \). The number of subclasses (subsets) after each \( n \)-th step will then be equal to \( P_{n+1} = P_n - 1 \). After carrying out \( m-q \) steps, we achieve breakdown into \( q \) subclasses. We thus obtain a classification into the previously given number of subclasses. In our case, however, the number of subclasses is unknown, and the optimum number is to be determined.

We define the average characteristic potential of the breakdown into \( q \) subclasses as

\[
    \Psi_1 = \frac{1}{q} \sum_{i=1}^{q} \varphi(y_i, y_i),
\]

and the average external potential of the breakdown as

\[
    \Psi_2 = \frac{2}{q(q-1)} \sum_{i=1}^{q} \sum_{j=i+1}^{q} \varphi(y_i, y_j).
\]

\( \Psi_1 \) provides a measure of the similarity of the points in the subclasses on the average for a given \( q \), and \( \Psi_2 \) provides a measure of the similarity of the subclasses to one another for a given \( q \). It is obvious that the optimum \( q \) will correspond to the maximum value of the difference \( \Psi_1 - \Psi_2 \), that is,