# CHEMISTRY

I. B. BERSUKER

1960

SovietRxiv

## Abstract

## Full Text

*CHEMISTRY*

I. B. BERSUKER

# ON THE QUESTION OF THE SYMMETRY OF COMPLEX COMPOUNDS

*(Presented by Academician A. A. Grinberg, 11 I 1960)*

The symmetry of the spatial arrangement of ligands around the central ion determines, as is known, the majority of the physicochemical properties of complex compounds. These include, for example, magnetic properties, optical activity, the character of the infrared spectrum, the number of bands of long-wavelength (electronic) absorption, the number of isomers, etc. In investigating these properties it is found that the best agreement with experimental data for most complex compounds is obtained if it is assumed that their symmetry, even in the case of identical ligands, is not the highest possible for the given coordination number ([1–4], etc.). This is also confirmed by direct electron-diffraction and X-ray measurements ([5–7], etc.).

Deviations from the highest symmetry, although usually not very large, do not follow directly from existing theories of coordination-bond formation, but find a fundamental explanation on the basis of the theorem on the stability of nonlinear polyatomic molecules proposed by Jahn and Teller ([8]). According to this theorem, a complex of the type $AB_n$ may, at the highest symmetry, prove to be unstable; moreover, the methods of group theory ([9]) make it possible to decide the question of the types of symmetry among which one should seek its stable configuration. Such a qualitative explanation of the observed "asymmetries" is in practice not very effective, since it gives no data either on the character of the deviations from the highest symmetry or on their magnitude. Therefore a quantitative calculation, which would give an idea of the real spatial arrangement of the ligands around the central ion and an approximate quantitative characterization of the deviations of the ligand positions from the positions of maximum symmetry, seems to us timely. The results of such a calculation are presented in the present communication.

The calculation was carried out in the approximation of ion–ion or ion–dipole interaction between the central ion $A$ and the ligands $B$. In this approximation the total (adiabatic) interaction energy $E(R_i)$ in a complex of the type $AB_6$, with configuration $A - d^n$ (over a closed shell) and with arbitrary positions of the ligands $B$, can be divided into two parts (to within a constant):

$$E(R_i) = W(R_i) + \varepsilon(R_i). \tag{1}$$

Here $W(R_i)$ is the interaction energy of the spherically symmetric core of the central ion with the ligands and of the ligands with one another, while $\varepsilon(R_i)$ is the averaged interaction energy of the $d$-electrons with the ligands. The asymmetry in the arrangement of the ligands is in fact due to the nonsphericity of the electron cloud of the $d$-electrons. Therefore we shall assume that, under the influence only of the spherically symmetric closed core of the central ion, the complex would be strictly octahedral, with positions

of ligands at the points $R'_{0i}(R'_0, \vartheta'_{0i}, \varphi'_{0i})$

$$\vartheta_{01} = 0, \qquad \vartheta_{06} = \pi, \qquad \vartheta_{02} = \vartheta_{03} = \vartheta_{04} = \vartheta_{05} = \pi/2,$$

$$\varphi_{02} = 0, \qquad \varphi_{03} = \pi/2, \qquad \varphi_{04} = \pi, \qquad \varphi_{05} = 3\pi/2.$$

These points, consequently, are points where

$$\left(\frac{\partial W}{\partial R_i}\right)_{R_i = R'_{0i}} = 0. \tag{2}$$

Our task is to find the equilibrium positions of the ligands $R_{0i}$ from the condition of a minimum of the total potential energy $E(R_i)$:

$$\left(\frac{\partial E}{\partial R_i}\right)_{R_i = R_{0i}} = \left(\frac{\partial W}{\partial R_i}\right)_{R_i = R_{0i}} + \left(\frac{\partial \varepsilon}{\partial R_i}\right)_{R_i = R_{0i}} = 0. \tag{3}$$

To find the dependence $\varepsilon = \varepsilon(R_i)$ we assume that the interaction of the ligands with the $d$-electron

$$V = q \sum_{i=1}^{6} \frac{1}{|\mathbf{r} - \mathbf{R}_i|} \tag{4}$$

is a small perturbation ($q$ is the charge of the ion; the transition to dipole ligands causes no additional difficulties).

Expanding $V$ in a series in spherical functions and, in the central-field approximation, using the 5 $d$-functions

$$\Psi_m = f(r) Y_2^m(\vartheta, \varphi), \qquad m = 2, 1, 0, -1, -2, \tag{5}$$

it is easy to obtain the matrix elements:

$$V_{mm'} = q\sum_{i=1}^{6}\left[A_{mm'}F_4(R_i)Y_4^{m-m'}(\vartheta_i,\varphi_i) + B_{mm'}F_2(R_i)Y_2^{m-m'}(\vartheta_i,\varphi_i) + \right.$$

$$\left. + C_{mm'}F_0(R_i)Y_0^{m-m'}(\vartheta_i,\varphi_i)\right]. \qquad (6)$$

Here

$$F_k(R) = \frac{1}{R^{k+1}}\int_0^R r^k f^2(r)\,dr + R^k\int_R^\infty \frac{1}{r^{k+1}} f^2(r)\,dr, \qquad (7)$$

and the constants $A_{mm'}$, $B_{mm'}$, and $C_{mm'}$ are expressed simply through Clebsch–Gordan coefficients.

In the case of the configuration $d^1$ (a central ion of the type $\mathrm{Ti}^{3+}$), the secular determinant formed from the matrix elements (6) leads to an equation of the fifth degree in $\varepsilon$. Its solution in general form is hardly possible. But one can make use of the fact that in a field of tetragonal symmetry the secular equation is solved exactly. In this case the lowest levels are either the doubly degenerate $E$ with energy $\varepsilon_{12} = V_{11}$, if the tetragonal symmetry arises from the lengthening of one of the diagonals of a regular octahedron (an elongated octahedron), or the nondegenerate $A_{2g}$ with energy $\varepsilon_3 = V_{22} - V_{2-2}$, if this symmetry arises from shortening of the diagonal (a compressed octahedron). One may then separately* investigate the behavior of the levels $E_g$ and $A_{2g}$ (in a cubic field both merge into $T_{2g}$) in the field of arbitrarily arranged ligands. The first of them splits into two with energy $\varepsilon_{12} = V_{11} \pm |V_{1-1}|$, which gives for the lowest electronic term

$$\varepsilon_1 = V_{11} - |V_{1-1}|. \qquad (8)$$

* This is equivalent to neglecting the matrix elements arising from wave functions of different levels. They are equal to zero for symmetry up to and including $C_{2v}$.

Substitution of (8) into (3), taking account of (6) and (2), gives:

$$\vartheta_{01} = 0, \quad \vartheta_{06} = \pi, \quad \vartheta_{02} = \vartheta_{03} = \vartheta_{04} = \vartheta_{05} = \pi/2, \quad \varphi_{02} = 0, \quad \varphi_{03} = \pi/2,$$

$$\varphi_{04} = \pi, \quad \varphi_{05} = 3\pi/2, \quad R_{01} = R_{06} = R_{02} = R_{04}, \quad R_{03} = R_{05},$$

with $R_{03} < R_{01}$. Hence it is seen that the equilibrium positions of the ligands correspond to tetragonal symmetry*, in which the ligands are situated at the vertices of an octahedron shortened along one diagonal. The electronic term will be $A_{2g}$. The same result is obtained if one starts from the level $A_{2g}$ from the very beginning.

One can derive a formula relating the difference of the lengths of the diagonals $\xi = 2(R_{01} - R_{03})$ to the force constants of the complex. Taking $\xi$ to be a small parameter, we may expand $E$, $W$, and $\varepsilon$ in series in $\xi$ and retain in them only terms up to and including squares. Then the conditions for a minimum of the total energy (3) give

$$\xi = \frac{2}{21}\, q\, \frac{5F_4''(R_{01}) - 9F_2''(R_{01})}{k - 2h + l}. \tag{9}$$

Here primes denote derivatives; $k$, $h$, and $l$ are the force constants of the complex: $k$ is the fundamental constant of elastic bonding, $h$ is the constant of "interaction" of two adjacent bonds, and $l$ is the constant of interaction of a bond with the opposite one ($h$ and $l$ are small in comparison with $k$, so that they can often be neglected). On substituting reasonable values of the parameters into (9), the magnitude $\xi$ is obtained of the order of 0.5 Å.

If the ligands are not ions but dipoles with dipole moment $\mu$, then

$$\xi = -\frac{2}{21}\, \mu\, \frac{5F_4''(R_{01}) - 9F_2''(R_{01})}{k - 2h + l}. \tag{10}$$

For complexes $AB_6$ with configuration $A$—$d^9$ (one $d$-hole in the filled $d^{10}$ shell—an ion of the type $\mathrm{Cu}^{++}$), it is necessary to investigate the level $E_g$ with energy $\varepsilon = V_{00}$, which in a cubic field is the lowest. The condition for a minimum of the total energy predicts tetragonal symmetry for these complexes as well**, but they may be either shortened or elongated octahedra. In both cases

$$|\xi| = -\frac{1}{14}\, q\, \frac{12F_2'(R_{01}) + 5F_4'(R_{01})}{k - 2h + l} \tag{11}$$

for ionic ligands, and

$$|\xi| = \frac{1}{14}\, \mu\, \frac{12F_2''(R_{01}) + 5F_4''(R_{01})}{k - 2h + l} \tag{12}$$

for dipole ligands. The order of magnitude of the distortion of the octahedron here is considerably greater ($\sim$ 3 times) than in the case of complexes with configuration $d^1$, and, consequently, $\xi$ may attain a very substantial value. This, apparently, explains the known structure of the complex $\mathrm{Cu(H_2O)_5SO_4}$, in which 4 water molecules are at a considerably shorter distance than the remaining ligands.

For the configuration $d^2$ (an ion of the type $V^{3+}$), the wave functions (5) must be antisymmetrized in the corresponding manner. In this case the matrix elements of the secular equation are expressed linearly through the matrix elements (6). The complexes $AB_6$ in this case also prove to be tetragonal, and for an elongated octahedron

$$\xi = \frac{1}{70}\, q\, \frac{24F_2'(R_{01}) - 25F_4'(R_{01})}{k - 2h + l}. \tag{13}$$

* This result confirms the general conclusions of work (10).

** The author recently became aware of work (11), in which an analogous case is discussed.

However, complexes of the type $AB_4$ have the highest possible symmetry, i.e., they will be regular tetrahedra.

For the configuration $d^8$ (two $d$-holes, an ion of the $Ni^{++}$ type) the situation is the reverse: complexes of the type $AB_6$ will possess the highest cubic symmetry, i.e., will be regular octahedra, whereas complexes $AB_4$ will not possess the maximal symmetry of a tetrahedron, but will be tetragonal with the planar structure of a square. These conclusions are confirmed by extensive experimental data.

It should be noted that the conclusions we have obtained concerning the symmetry of complexes have general significance, independent of the assumed type of bonding in them. As for formulas (9)–(13), they can serve as a quantitative characteristic of the distortion of the highest symmetry in a complex only to the extent that the real bonds in it approximate electrostatic ones; to the same extent they can serve for calculating force constants, if the distances between the central ion and the ligands have been measured.

In conclusion I express my sincere gratitude to A. V. Ablov, M. G. Veselov, Yu. E. Perlin, and T. I. Malinovskii for valuable discussions.

Bălți State
Pedagogical Institute

Received
8 I 1960

## CITED LITERATURE

1. J. H. van Vleck, Phys. Rev., **41**, 208 (1932).

2. R. Schlapp, W. G. Penney, Phys. Rev., **41**, 194 (1932); **42**, 666 (1932).

3. O. Redlich, T. Kurz, W. Stricks, Monatsh. f. Chem., **71**, 1 (1937).

4. J. Czászár, J. Balog, L. Lehotai, Acta phys. et chem. Szeged, **2**, 56 (1956).
5. H. Braune, P. Pinnow, Zs. phys. Chem., **35**, 232 (1937).
6. H. Bode, H. V. Döhren, Acta Cryst., **11**, 80 (1958).
7. J. Dunitz, L. E. Orgel, J. Phys. Chem. Solids, **3**, 20 (1957).
8. H. A. Jahn, E. Teller, Proc. Roy. Soc., A **161**, 220 (1937).
9. H. Bethe, Ann. d. Phys., **3**, 133 (1929).
10. U. Öpik, M. H. L. Pryce, Proc. Roy. Soc., A **238**, 425 (1957).
11. A. D. Liehr, C. J. Ballhausen, Ann. Phys. USA, **3**, 304 (1958).

*Note: Figure translations are in progress. See original paper for figures.*