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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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On Two Conformations of Some Inorganic Complexes of Transition Metals

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In the present communication we draw attention to the possibility of the existence of two conformations (nonequivalent equilibrium configurations) of certain octahedral complexes of transition metals, principally analogous to the conformations of organic compounds, the study of which has been widely developed.

As is known, the equilibrium positions of ligands in six-coordinate complexes of transition metals are, generally speaking, displaced from the positions at the vertices of a regular octahedron even when all the ligands are identical. This internal asymmetry arises as a consequence of the asymmetry of the ψ-cloud of the d-electrons of the central atom and, as investigations show ([1,2]), is especially large for the electronic configurations d^9 (Cu(II), Ag(II), Au(III)), d^4 (Cr(II), Mn(III), Mo(II), W(II), Re(III))—in the high-spin state—and d^7 (Co(II), Rh(II), Ir(II))—in the low-spin state. It is essential that in these cases two types of equilibrium configurations are possible, which are not equivalent to each other. In both cases the equilibrium octahedron is tetragonally distorted, but in one of them one diagonal of the octahedron is longer than the other two (an elongated or stretched octahedron, Fig. 1, *I*), whereas in the other it is shorter (a shortened or compressed octahedron, Fig. 1, *II*). These two equilibrium configurations correspond to positions of minima of the potential-energy surface of the complex; since they are nonequivalent to each other, we shall call them configurations *I* and *II*, respectively. We shall show that there are substantial differences between them, which lead to interesting consequences.

Fig. 1

The most essential characteristic of a conformation is its energy. In calculating the energy of complexes we usually represent it as the sum of two parts ([2]): the energy of interaction of the optical electrons of the central ion* with the ligands and the energy of the remaining interactions in the basis. Whereas the first part of the energy is calculated rather accurately, the second part is approximated with the aid of force constants. In doing so it is assumed that the potential well for the ligands is strictly symmet—

* In the approximation of the molecular-orbital method the general picture and the results are analogous.

with a parabolic curve (the vibrations of the ligands are harmonic). In this approximation the energy of both conformations *I* and *II* is the same. However, if one takes into account the asymmetry introduced by the cubic term in the expansion of the potential energy in ligand displacements from the equilibrium positions (i.e., the anharmonicity of the vibrations), then the energies of the two conformations turn out to be different. Since anharmonicity introduces into the energy a correction not exceeding a few percent, the order of magnitude of the energy difference between the two conformations should be the same. An estimate shows that the energy of conformation *II* is higher than the energy of conformation *I* by several percent of the characteristic energy of formation of the conformation—the lowering of the energy upon transition from a regular octahedron to a distorted one (20-30 kcal/mol), which is of the order of 1 kcal/mol. This estimate of the energy difference between conformations *II* and *I* is very rough, which, however, does not diminish the further qualitative conclusions.

With such an energy difference, the concentration of complexes in conformation *I* under equilibrium conditions will be approximately 10 times greater than the concentration of conformation *II*, which is readily established with the aid of the Boltzmann distribution.

The next important characteristics of a conformation are the magnitude of the internal asymmetry $\xi = 2(R_{01} - R_{02})$ (the difference between the lengths of two diagonals), the energy and symmetry of the electronic states, and also the frequency of hindered motions—transitions between the three equivalent states with different directions of asymmetry (along the diagonals 1-4, 2-5, and 3-6). Methods for determining these quantities, general formulas, and calculations for some aquo complexes were given by us in previous communications ([1−3]). From these formulas one can also determine the height of the barrier for each conformation—the energy difference of the complex in the state of a regular octahedron and in the state of the given conformation. Knowing the barrier heights, one can determine the frequency of transitions between conformations and the lifetime of each of them, similarly to how these quantities are determined for hindered motions ([3]).

We give the characteristics of the conformations calculated in this way for the example of $[Cu(H_2O)_6]^{2+}$: the magnitude of the internal asymmetry $\varphi = 2(R_{01} - R_{02})$ is 0.8 Å (*I*) and −0.8 Å (*II*); the energy difference of conformations *II* and *I* is $\sim$ 1 kcal/mol; the concentration ratio $II : I$ at equilibrium at ordinary temperatures is ~ 0.1; the height of the potential barrier between conformations is ~ 15 (*I*) and ~ 14 kcal/mol (*II*); the lifetime in the ground state is ~ 4 days (*I*) and ~ 3.3 hours (*II*); the difference in the bond energies of ligands 1 and 2 is ~ -15 (*I*) and ~ 15 kcal/mol (*II*).

From these data we see that the lifetimes of the conformations are sufficiently long for each conformation to be regarded as an independent chemical object (in calculating the lifetimes of the conformations we assumed that the corresponding vibrational frequency of the complex is equal to 250 cm^{-1}).

Of interest are the results of an approximate calculation of the difference in bond energies of ligands on the long and short diagonals, respectively. Such a difference can be obtained from the explicit form of the energies of the optical electrons in the ligand field ([1,2]), taking into account the correction for the difference in changes in core energy upon detachment of ligands 1 and 2. As was to be expected, the ligands on the long diagonals are bound more weakly than those on the short ones; the difference in bond energies in these two cases, for example for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, is of the order of 15 kcal/mol. For configuration *I*, therefore, two ligands in trans positions 1 and 4 are bound considerably more weakly than the other four ligands 2, 3, 5, and 6; and for conformation *II* these latter four ligands are bound more weakly than the first two. At the same time, both the nearby and the distant ligands of conformation *II* are bound more strongly (by an amount of the order of 5 kcal/mol for the example $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$) than, respectively, the nearby and distant ligands of conformation *I* (in this case the energy of conformation *I* is not higher than *II*, since in the latter case there are four distant

weakly bound ligand, whereas in the case of I there are only two of them). This is one of the most substantial differences between the two conformations, which undoubtedly must affect the reactivity of the indicated complexes.

Let us consider an example. Suppose that the substitution reaction of a Cu(II) complex with identical ligands (for example, an aquo complex) proceeds by the S_N1 mechanism. Then, for the predominant conformation I, because of the substantially weak bond of ligands 1 and 4, they will inevitably be substituted first. This apparently can explain the clearly expressed tendency of Cu(II) toward the formation of trans-substituted complexes. It is possible that, upon detachment of two ligands 1 and 4, substitution of only one of them is sufficient for stabilization of the complex. Then the pyramidal coordination characteristic of Cu(II) complexes is also formed. (The same considerations are probably also applicable to substitution by the S_N2 mechanism.) As for conformation II, for it, in principle, both trans- and cis-substitution are possible. But, first, conformation II is less reactive than I because of the stronger bonding of the individual ligands in it; second, at ordinary temperatures its concentration is significantly smaller. In addition, cis-substitution is further hindered by the fact that, after the detachment of one weakly bound ligand, for example 2 (Fig. 1, II), the most favorable conditions for detachment are created for the ligand in the trans position 5. If, however, substitution proceeds stepwise, then, with a sharp difference between the replaced and replacing ligands, the latter introduces a strong perturbation that can convert the complex from conformation II into the more stable conformation I, with subsequent trans-substitution. However, for some reactions it apparently is possible to create conditions under which cis-substitution will occur (an increase in the concentration of conformation II with increasing temperature, substitution of ligands by quasi-identical ones—labeled or identical in the part attached to the central atom, etc.).

Among other possible manifestations of the existence of two conformations, we point to relaxation phenomena leading to additional absorption of ultrasound as it passes through a solution of a complex compound (analogous additional absorption of ultrasound is observed for conformations of organic compounds ([4])). Certain possibilities for distinguishing the two conformations are also presented by data on light absorption ([5]).

The investigation of the questions raised in the present communication awaits further development and experimental verification.

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