ON THE STRUCTURE OF THE COMPLEX ION $[\mathrm{OsNCl}_5]^{2-}$

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Abstract

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ON THE STRUCTURE OF THE COMPLEX ION $[OsNCl_5]^{2-}$

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G. B. Bokii, L. O. Atovmyan, and T. S. Khodashcheva (^{1}) investigated the structure of the crystals K_2OsNCl_5 and $KOsNBr_4 \cdot 2H_2O$ and found that in the octahedral complex ions $[OsNCl_5]^{2-}$ and $[OsNBr_4(H_2O)]^-$ the Os—N distance is very short (~ 1.60 Å); and in the first of these ions the Os—Cl distances are not identical—four chlorine atoms in the equatorial plane are at distances of 2.4 Å, close to the sum of the covalent radii, whereas the distance to the fifth chlorine atom (in trans-position to the nitrogen atom) is greatly shortened (2.1 Å). At the same time, in the ion $[OsNBr_4(H_2O)]^-$ the distance to the H_2O molecule in trans-position to the nitrogen atom is normal.

To explain the observed anomaly in the bonds in $[OsNCl_5]^{2-}$, we considered, by means of group theory, the possibilities for formation of bonds between the central atom and the ligands in this complex ion. The structure of the ion $[OsNCl_5]^{2-}$, which belongs to the symmetry group C_{4v}, is shown in Fig. 1. We took as the z-axis the C_4 axis coinciding with the NOsCl line, and as the x and y axes the ClOsCl lines in the equatorial plane. Table 1 gives the assignment of the atomic orbitals of the central atom and

Table 1

Assignment of the atomic orbitals of the central atom and the ligand orbitals to the irreducible representations of the group C_{4v}

Orbitals	A_1	A_2	B_1	B_2	E
Atomic orbitals of the central atom	s, p_z, d_{z^2}	—	$d_{x^2-y^2}$	d_{xy}	$p_x, p_y d_{xz}, d_{yz}$
σ-orbitals of 4 Cl atoms in the equatorial plane	σ_1		σ_2		σ_3, σ_4

Fig. 1

Figure 1: Fig. 1

Orbitals	A_1	A_2	B_1	B_2	E
Orbitals of the N atom	$\sigma(p_z)\sigma_N\pi(p_x,p_y)$				π_{N1},π_{N2}
Orbitals of the Cl atom in trans-position to the N atom	$\sigma(p_z)\sigma_{\mathrm{Cl}}\delta(d_{xy})$			δ_{Cl}	

ligand orbitals to the irreducible representations of the symmetry group. The σ-orbitals of the four Cl atoms in the equatorial plane are formed by the p_x-orbitals of two Cl atoms situated on the x-axis and the p_y-orbitals of two Cl atoms on the y-axis. As is seen from Table 1, they interact with formation of four σ-bonds Os—Cl with a square configuration with the $d_{x^2-y^2}sp_xp_y$-orbitals of Os. In addition to the indicated σ-bonds, there are two more σ-bonds between Os and the ligands along the z-axis (N and Cl) through the p_z-orbital of N and Cl and the hybrid $p_zd_{z^2}$-orbitals of Os. The choice of orbitals for these σ-bonds is unambiguous—

chen. Other d-orbitals are not suitable for the formation of σ-bonds. But the possibilities for formation of bonds of Os with ligands are not exhausted by the formation of σ-bonds alone, since nitrogen has two more unpaired electrons (in the p_x and p_y orbitals of symmetry E), which can give two π-bonds with the d_{xz}, d_{yz}-orbitals of Os (of the $d\pi$—$p\pi$ type), so that the Os—N bond is triple. This is what determines the short distance between Os and N. In this case also, for the second and third components of the Os bond only the d_{xz}, d_{yz}-orbitals can be used.

⊙—Os atom ●—N atom ∘—Cl atoms

Fig. 1

For the formation of all the bonds described, Os must have 8 unpaired electrons in the orbitals $d_{x^2-y^2}sp_xp_yp_zd_{z^2}$ (for σ-bonds), and d_{xz}, d_{yz} (for π-bonds with N). In addition, if the Cl and N atoms form respectively one and three bonds with Os, the charge of the complex ion (2—) is formally located on the Os atom*.

In this case the Os atom is in a state that makes possible the formation of all the bonds listed.

$$\begin{array}{ccccccccc} d_{xy} & d_{xz} & d_{yz} & d_{z^2} & d_{x^2-y^2} & s' & p_x & p_y & p_z \\ \downarrow\uparrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \end{array}$$

$$\underbrace{\qquad\qquad\qquad}_{\pi\text{-bonds with N}} \quad \underbrace{\qquad\qquad\qquad}_{\sigma\text{-bonds with N and Cl in trans position}} \quad \underbrace{\qquad\qquad\qquad}_{\sigma\text{-bonds with Cl in the equatorial plane}} \quad \underbrace{\qquad\qquad\qquad}_{\sigma\text{-bonds with N and Cl in tran}}$$

Usually, consideration of bonds in Os complexes containing a nitrogen atom is limited to the above considerations concerning the formation of ordinary bonds between Os and all the Cl atoms and a triple Os N bond. But this does not make it possible to explain the difference in the Os—Cl distances in the equatorial plane and along the z axis. We believe that an approach to explaining this feature of the ion $OsNCl_5^{2-}$ is possible if one takes into account the possibility of the formation of additional bonds between the Cl atoms and the central atom at the expense of the lone pair of Os electrons and a vacant d-orbital of Cl in the trans position. (We do not consider the possibility of forming π-bonds at the expense of lone pairs of p-electrons of the Cl atoms and vacant orbitals of the central atom, owing to the absence of vacant orbitals in Os.) As is evident from the preceding, Os still has a d_{xy} orbital occupied by a pair of electrons, belonging to the irreducible representation B_2. This means that if the atom Cl_{trans} has an empty orbital of the same symmetry, an additional bond can arise between them. In the Cl atom all the $3d$-orbitals are empty, but of these only the $3d_{xy}$-orbital belongs to the representation B_2 (for the symmetry of the complex ion C_{4v}). Between the d_{xy}-orbitals of two interacting atoms, bonds of three types are possible in principle: σ (with overlap of two lobes of the functions—one from each orbital), π (with overlap of four lobes—two from each orbital), and δ (with overlap of all eight lobes) (^{2}). In the case we are considering, the two d_{xy}-orbitals (of the Os and Cl atoms) are located in parallel planes. In this situation, effective overlap between them is possible only with formation of a bond

* Owing to the partly ionic character of the Os—Cl bonds and the π-bonds OsN, the charge is in fact distributed over all the atoms, but this is not essential for a group-theoretical consideration of the possibility of bond formation.

of the δ type, while the conditions for the formation of a σ or π bond are considerably less favorable.

With Cl atoms in the plane, δ bonds cannot be formed, since the Os orbitals required for this (d_{xz} and d_{yz}) are already occupied in the multiple bond with N. In the octahedral complexes $OsCl_6^{2-}$ and $OsBr_6^{2-}$, formation of a δ bond with any of the halogen atoms along all three axes x, y, z is equally probable. But for these bonds the central atom can provide only one pair of electrons (in these complexes two Os electrons remain unpaired), so that each OsCl bond accounts for a 1/6 share of a δ bond. Thus, in $OsNCl_5^{2-}$ the Os—Cl bonds in the plane are purely ordinary; in $OsCl_6^{2-}$ the Os–Cl bonds contain only a small admixture of δ bonding. Therefore the bonds of these two types are close in length.

In contrast to the preceding ones, the Os—Cl_{trans} bond in $OsNCl_5^{2-}$ is multiple, consisting of σ and δ components. The presence of this additional δ component in the bond is, in our opinion, the reason for the shortening of this distance.

The condition for the appearance of an additional bond between the O atom and the atom in the trans position to N is the presence in the trans atom of a free d_{xy} orbital (the s or p orbitals under C_{4v} symmetry do not belong to the representation B_2, to which the Os orbital unused for σ bonds and π bonds with N belongs). Such a free orbital, close in energy to the orbitals occupied in the bonds, can occur only in atoms of the 3rd period of the Mendeleev periodic system, but not in atoms of the second period. Therefore, whereas Cl can give an additional δ bond with Os, F or O atoms cannot give such a bond, and the Os–O bond in $[OsNBr_4OH_2]^-$ or the Os–F bond in $[OsNF_5]^{2-}$ must be simply ordinary σ bonds. This conclusion agrees with the fact that, according to data (1), the Os–O distance in $[OsNBr_4OH_2]^-$ is normal. It may be assumed that the Os—F_{trans} distance in $[OsNF_5]^{2-}$ also should not differ noticeably from the other Os–F distances.

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CITED LITERATURE

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