

## EHMO Study on the Solvation Site in the System [Co(CN)<sub>6</sub>]<sup>3-</sup>-H<sub>2</sub>O

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The outersphere coordination (solvation) of the cyano metal complexes has already been investigated in some fields [1] of coordination chemistry as well as the innersphere coordination of solvent molecules. The complex  $K_3[Co(CN)_6]$  is one of the most familiar cyano metal complexes. The author has investigated the electronic absorption spectrum, <sup>59</sup>Co NMR and <sup>13</sup>C NMR of this outersphere cobalt(III) complex in a variety of solvents [2]. It was reported in this work that the protic solvent molecules interact with the  $C\equiv N^-$  ligand through hydrogen bonding. However, detailed information about the structure of this outersphere complex was not available. This is because the outersphere coordination of solvent molecules is flexible and is not rigid, which is quite different from the innersphere coordination. It is also impossible to determine this structure by X-ray analysis. The structure in the solid state should be different from that in solution even if the hydrate salt of this complex anion is available.

However, it is quite important to know how the solvent molecules interact with the innersphere complex,  $[Co(CN)_6]^{3-}$ . The site of the interaction could decide the spectral properties or reaction mechanisms. In our previous work [2], the solvent influence on the electronic absorption spectrum and the <sup>59</sup>Co NMR of  $[Co(CN)_6]^{3-}$  could be reasonably clarified if the solvent molecules interact with the  $\pi$  electrons of the innersphere ligand  $C\equiv N^-$ .

From this viewpoint, a preliminary attempt is made to determine the detailed structure of the  $[Co(CN)_6]^{3-}-H_2O$  complex by use of the extended Hückel MO (EHMO) calculation. The EHMO method is widely used for the examination of the structures and reactivities of many metal complexes [3]. It has been reported in the literature that the results of these calculations are quite informative on the correlation between potential energy and the bond angles of metal complexes, despite the approximate nature of the computational method. In the present work, we investigate whether (i) the water molecule prefers the carbon or nitrogen atom of the innersphere ligand  $C\equiv N^-$ , and whether (ii) the water molecule prefers the  $\sigma$ -electron or  $\pi$ -electron of the ligand nitrogen, where the hydrogen bonding between the water hydrogen and innersphere ligand  $C\equiv N^-$

TABLE 1. Parameters used in extended Hückel calculations

Atom	Orbital	$H_{ii}$ (eV)	Exponents <sup>a</sup>		Coefficients <sup>a</sup>	
			$\xi_1$	$\xi_2$	$C_1$	$C_2$
Co	3d	-13.18	5.55	2.10	0.568	0.606
	4s	-9.21	2.00			
	4p	-5.29	2.00			

<sup>a</sup>Coefficients and exponents in a double  $\xi$  expansion.

is postulated in the outersphere coordination (solvation).

All calculations were performed by use of the extended Hückel method described by Hoffmann. Program number QCPE No. 0344 from the Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, was used at the Computer Center of the Institute for Molecular Science. The off-diagonal elements  $H_{ij}$  were calculated by a weighted Wolfsberg-Helmholtz formula with the standard  $K$  value of 1.75. The Coulomb integrals and orbital exponents for Co are listed in Table 1 [4] and the parameters for C, N, O and H are the standard ones. Charge iterations were performed on the hydration models of  $[Co(CN)_6]^{3-}$  (1:1 hydration of  $[Co(CN)_6]^{3-}$  with  $H_2O$ ), assuming a linear charge dependence for  $H_{ii}$  ( $H_{ii} = H_{ii} + 2q$ ). Geometrical assumptions included are as follows: Co-C, 1.90 Å; C-N, 1.15 Å; O-H, 0.96 Å; C-Co-C (*cis*), 90°; C-Co-C (*trans*), 180°; Co-C-N, 180°; H-O-H, 104.5°; the distance of the hydrogen bonding between the water hydrogen and the cyano nitrogen is assumed to be 1.72 Å.

At first, we examined by the EHMO calculation which atom is solvated (hydrogen-bonded) by the water molecule, carbon or nitrogen. Quantitative EHMO calculations were performed on the model system that is shown in Fig. 1. The distance to the water hydrogen from the line of Co-C-N, which is also presented in Fig. 1, is taken as a variational parameter and is varied from 1.90 to 3.05 Å. The relationship of the change in total energy for the structure of this model with the distance  $d$  is shown in Fig. 2. It is clear in this Figure that total energy decreases as the distance becomes longer and is the lowest at 3.05 Å in this range of the distance. A water

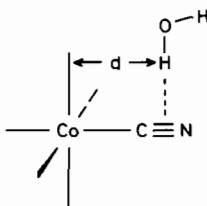


Fig. 1. Solvation model A for the system  $[Co(CN)_6]^{3-}-H_2O$ .

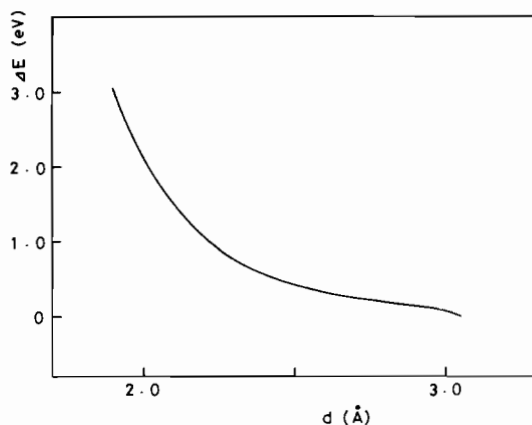


Fig. 2. The change in total energy for the structure of model A with distance  $d$ .

molecule at this position interacts with the  $p_z(\pi)$  electron of the cyano nitrogen. This suggests that the hydrogen-bonded solvation of this type is the most strongly formed between the water hydrogens and the  $\pi$ -electron belonging to the cyano nitrogen. At this stage, it was concluded that the water molecules predominantly interact with the nitrogen atom or the electrons which exist near the nitrogen in the  $\pi$ -molecular orbital of  $C\equiv N^-$  (there exists 2.5–3.0 eV (50–60 kcal/mol) energy difference between these positions and that for carbon atom at 1.90 Å).

Suppose that the water hydrogen interacts with the cyano nitrogen. The next problem is to decide the direction of the solvation for the cyano nitrogen. EHMO calculations were carried out on the model that is shown in Fig. 3. In this model, the angle C–N–H ( $\theta$ ) is taken as a variational parameter that is presented in Fig. 3 and is varied from  $90^\circ$  to  $-90^\circ$ . In Fig. 4 is shown the relationship of the change in total energy for the structure of this model with the angle  $\theta$ . In this case, there seem to exist five minima at the angle  $\theta$  near to  $60^\circ$ ,  $30^\circ$ ,  $0^\circ$ ,  $-30^\circ$  and  $-60^\circ$  in the range from  $90^\circ$  to  $-90^\circ$ . This result is somewhat surprising because this cyano ligand ( $C\equiv N^-$ ) forms the  $sp$ -hybrid orbital according to the valence bond theory and the lobes of the orbitals that belong to cyano nitrogen and could form the hydrogen bonding with the water hydrogen are directed to the directions  $\theta = 0^\circ$  and

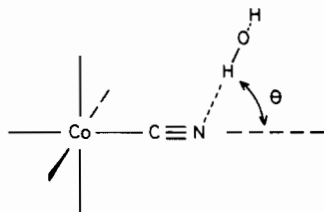


Fig. 3. Solvation model B for the system  $[Co(CN)_6]^{3-}-H_2O$ .

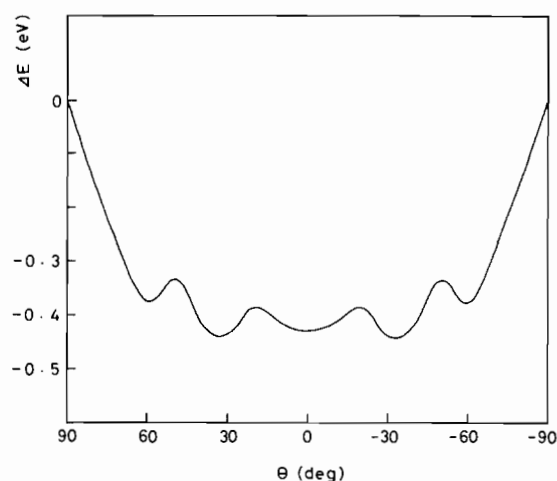


Fig. 4. The change in total energy for the structure of model B with the C–N–H angle ( $\theta$ ).

$90^\circ$  that correspond to the  $\sigma$ -electron and  $\pi$ -electron lobes, respectively. The result of five minima seems to suggest that a  $C\equiv N^-$  nitrogen has a character of a partial  $sp^2$ -hybridization like  $Co=C=N^-$  when the cobalt(III) complex forms. The directions of  $60^\circ$  ( $-60^\circ$ ) and  $0^\circ$  correspond to those of the lobes of  $sp^2$   $\sigma$ -electrons and  $sp$   $\sigma$ -electrons, respectively. The midpoint ( $\theta = 30^\circ$  or  $-30^\circ$ ) of the deepest energy minimum is the site at which the hydrogen bonding should be formed by these two lobes.

Eventually, these EHMO results suggest that a water hydrogen interacts with the cyano nitrogen along the direction of the angle  $\theta$  ranging from  $60^\circ$  to  $-60^\circ$  and with the  $\sigma$ -electron lobes of the  $C\equiv N^-$  nitrogen.

Therefore, the interaction with the  $\sigma$ -orbital of  $C\equiv N^-$  could influence the  $\pi$ -molecular orbital between Co and coordinated carbon atom indirectly, and influence the UV,  $^{59}Co$  and  $^{13}C$  NMR spectra of  $[Co(CN)_6]^{3-}$  investigated by the author. The solvent molecules do not seem to interact to a great extent with the  $\pi$ -electrons of  $C\equiv N^-$  directly. A detailed and quantitative examination is in progress on the basis of the *ab initio* MO calculations.

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