

EHMO Calculation of $[\text{Co}(\text{ox})_2(\text{NH}_3)_2]^- - \text{H}_2\text{O}$ Solvation Model: Which Kind of Electron of Carboxylate Ligands is Preferred by Solvent Molecules, σ or π ?

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Solubilizing the potassium salts of cobalt(III) complexes in organic solvents by macrocyclic polyethers, the author found that the colors of some cobalt(III) complexes with carboxylate ligands change from solvent to solvent [1]. In this work, the following complexes are utilized: $\text{K}[\text{Co}(\text{edta})] \cdot 2\text{H}_2\text{O}$, $\text{K}[\text{Co}(\text{ox})_2\text{en}] \cdot 1.5\text{H}_2\text{O}$, $\text{K}[\text{Co}(\text{mal})_2\text{en}] \cdot \text{H}_2\text{O}$, $\text{K}_2[\text{Co}(\text{ox})_2\text{gly}] \cdot 3\text{H}_2\text{O}$ and $\text{K}_3[\text{Co}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$, where edta = ethylenediaminetetraacetate, ox = oxalate, en = ethylenediamine, mal = malonate and gly = glycine. These cobalt(III) complexes are quite stable and inert against ligand substitution or redox reaction under the conditions used, and thus it was concluded that this color change is due to the outer sphere interaction of the cobalt(III) complex anions with solvent molecules; the peak position (λ_{max}) of the first d–d absorption band is linearly correlated to the Gutmann's acceptor numbers of the solvents. Furthermore, as for the $[\text{Co}(\text{edta})]^-$ anion, this outer sphere interaction is found to be caused by the hydrogen bonding between the carboxylate oxygen of the complex anion and the hydrogen atom of the protic solvent (e.g. H_2O) on the basis of solvent dependence of the ^{13}C NMR of $[\text{Co}(\text{edta})]^-$ [2].

However, it is not exactly clear what kind of interaction with the ligand oxygen changes the peak positions of the first d–d transition bands of the cobalt(III) complex anions. The blue shift of the d–d transition spectra in the hydrogen-bonding solvent should be easily explained by the decrease of the contribution of the π orbital of the carboxylate oxygen [3], while the blue shift in the solvent influence is reported to correspond to the $n-\pi^*$ transition [4]. Therefore, as a first attempt to make this point clear, the author investigated which kind of electron of the ligand oxygens the water molecules preferentially interact with, σ or π , by using the extended Hückel MO (EHMO) calculations. In the present work, the complex $[\text{Co}(\text{ox})_2(\text{NH}_3)_2]^-$ (ox = oxalate) is used instead of $[\text{Co}(\text{ox})_2\text{en}]^-$ and other complex anions in order to simplify the EHMO calculation.

It has been reported in the literature that the results of EHMO calculations are quite informative

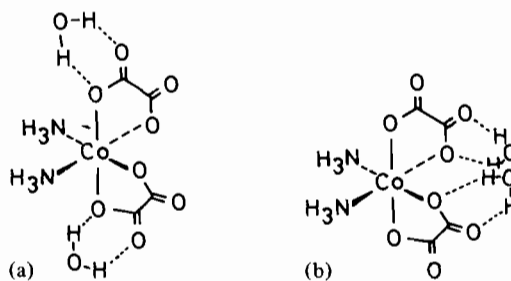
TABLE 1. Parameters used in extended Hückel calculations

Atom	Orbital	H_{ii} (eV)	Exponents ^a		Coefficients ^a	
			ξ_1	ξ_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			

^aCoefficients and exponents in a double- ξ expansion.

on the correlation between potential energy and bond angles of the metal complexes despite the approximate nature of the computational method. All calculations were performed using the extended Hückel method described by Hoffmann. Program number QCPE #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 [5] and the parameters for C, N, O and H are the standard ones. Charge iterations were performed on the hydration models of $[\text{Co}(\text{ox})_2(\text{NH}_3)_2]^-$ assuming a linear charge dependence for H_{ii} ($H_{ii} = H_{ii} + 2q$). Geometrical assumptions included are as follows: Co–N, 1.98; Co–O, 1.90; N–H, 1.02; C–O, 1.26; C=O, 1.23 Å; O=Co–O, 86°; N–Co–N, 90°; Co–O–C, 112°; O–C–C, 115°; O–C=O, 124°; C=O–H, 1.80; C–O–H, 1.95; C–O, 3.00; O–O, 2.60; O–H, 0.96 Å; H–O–H, 104.5°; NH_3 is assumed to have a tetrahedral geometry. $[\text{Co}(\text{ox})_2(\text{NH}_3)_2]^-$ is assumed to have C_2 symmetry.

Quantitative EHMO calculations were performed on the model systems which are shown in Fig. 1. The models used in this work are as follows: (a) two water molecules are hydrogen-bonded to the oxygens of two different carboxylates which are *cis* to NH_3 and (b) two water molecules are hydrogen

Fig. 1. Solvation models (a) and (b) for the system of $[\text{Co}(\text{ox})_2(\text{NH}_3)_2]^- - \text{H}_2\text{O}$.

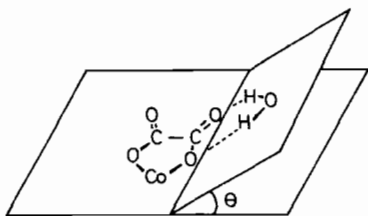


Fig. 2. The angle θ as a variational parameter. $\theta = 0^\circ$: solvation to the σ orbitals of the carboxyl oxygens. $\theta = 90^\circ$ or -90° : solvation to the π orbitals of the carboxyl oxygens.

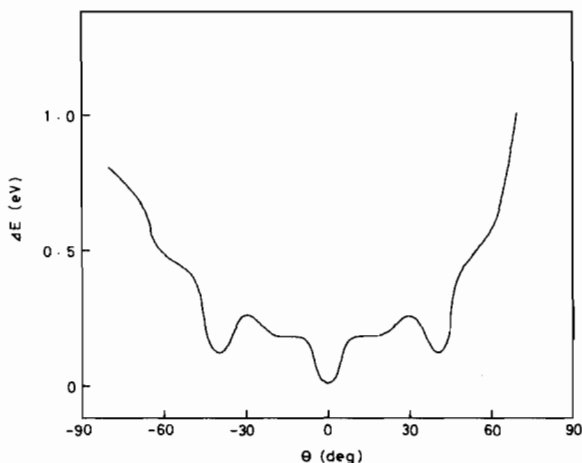


Fig. 3. The change in total energy for the structure of model (a) with the angle θ . Plus and minus signs mean that water molecules interact with carboxylate oxygens along the direction near the NH_3 and other oxalate ligands in Fig. 1, respectively.

bonded with two different carboxylates which are *trans* to NH_3 . This anion, $[\text{Co}(\text{ox})_2(\text{NH}_3)_2]^-$, is a singly charged anion and has a large ion-size like I^- or ClO_4^- , and thus this anion could work as a water-structure breaker [6]. Therefore, the water molecules near the complex anion could not form a cluster composed of some water molecules. Furthermore, it was reported on the basis of the conductance measurement [7] that the two hydrated water molecules solvate a $[\text{Co}(\text{mal})_2\text{en}]^-$ anion in aqueous solution. Accordingly, it seems reasonable to use these models with two solvated water molecules as hydration models of $[\text{Co}(\text{ox})_2(\text{NH}_3)_2]^-$. The angle θ that is presented in Fig. 2 is taken as a variational parameter and is varied from 90° to -90° . In Fig. 3 the relationship of the change of total energy for the model system (a) with the angle

θ is shown. In this case, there seem to exist three potential minima at the angle θ near to 40° , 0° and -40° . According to the valence bond theory, the carboxylate oxygens could have both characters of the sp^2 and sp^3 orbitals by the conjugation which is illustrated as $\text{O}=\text{C}=\text{O}$. The sp^2 σ orbital is directed to the direction of $\theta = 0^\circ$. The sp^3 σ orbital is directed to about $\theta = 60^\circ$ (or -60°). The angle 40° (or -40°) is near to a mid point of 0° and 60° (or -60°). This could be the reason why the energy minima of this model exist at the angles 40° , 0° and -40° and at the angles 60° and -60° , which appear as shoulders in Fig. 3. This suggests that water hydrogens interact with carboxylate oxygens along the direction of the angle θ ranging from about 40° to -40° and with the σ electron lobes of the COO^- oxygen.

As for model (b), the calculations showed the same trends as obtained for model (a) though the steric repulsion between two hydrated water molecules could be so pronounced.

It is concluded that the water molecules prefer the σ electron of the COO^- oxygen and interact with it along the direction of the angle θ ranging from 40° to -40° .

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