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POTENTIAL ENERGY SURFACE OF $[Cu(H_2O)_6]^{2+}$ AND $[Zn(H_2O)_6]^{2+}$ DERIVED FROM AB INITIO MO CALCULATIONS

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Ab initio molecular orbital calculations on $[Cu(H_2O)_6]^{2+}$ and $[Zn(H_2O)_6]^{2+}$ have been carried out to obtain the metal-oxygen bond lengths. The calculated results are in qualitative agreement with the expectation from the Jahn-Teller theorem; a distorted octahedron for Cu^{2+} and a regular octahedron for Zn^{2+}. However, the preference for an elongated octahedron observed in the Cu^{2+} complex was not shown by the present calculation.

Six-coordinate copper(II) complex is known to take distorted octahedral shapes, in accordance with the Jahn-Teller theorem.[1] Experimental evidence has been gathered by Reinen et al.[2] for the perference of elongation along the tetragonal axis. Recently, Yamatera[3] has shown that configuration interactions would probably stabilize the $^2B_{1g}$ ground state of the elongated octahedral complex to a greater extent than the $^2A_{1g}$ ground state of the compressed octahedral complex and that the 4s-$3d_{z^2}$ mixing would make a significant contribution to the energy difference between the $^2B_{1g}$ and $^2A_{1g}$ states. With an intention to obtain a deeper understanding of the stereochemistry of copper(II) complexes, we have performed ab initio molecular orbital calculations on the $[Cu(H_2O)_6]^{2+}$ ion, which is real, easy to be calculated, and of interest in solution chemistry. Calculations were also made on $[Zn(H_2O)_6]^{2+}$ for comparison. The structures of these ions in solution have been determined using the X-ray diffraction by Ohtaki et al.[4] and EXAFS by Sano et al.[5] as follows: $(Cu\text{-}O)_z$= 2.43 Å (4.595 a.u.) and $(Cu\text{-}O)_{x,y}$= 1.94 Å (3.667 a.u.), and $(Zn\text{-}O)_{x,y,z}$= 2.08 Å (3.932 a.u.).

The calculation was done in the SCF LCAO MO scheme with the basis set of Gaussian functions by using a program package JAMOL3 written by Kashiwagi et al.[6] The single-zeta basis sets are [10s,6p,3d/4s,3p,1d][7] for Cu and Zn, [7s,3p/2s,1p] for O, and [3s/1s] for H, respectively.[8] The ion was assumed to be D_{2d} symmetry and the interatomic distance between O and H was taken as 1.0 Å and the HOH bond angle 106.4°. The D_{2d} symmetry, which is D_{4h} minus the center of symmetry, is practically equivalent to D_{4h} in the present calculations which are concerned with gerade electronic states. Thirty and seventeen calculations, respectively, for the Cu and Zn complexes have been done with axial and equatorial metal-oxygen bond distances as variables. Figures 1 and 2 show the calculated potential energy surfaces for $[Cu(H_2O)_6]^{2+}$ and $[Zn(H_2O)_6]^{2+}$ ions, respectively. The error in the calculation of the total energies is less than 1×10^{-4} a.u. The digits given in

Figs. 1 and 2 are the last three significant figures of the total energy values, -2086.4___ and -2224.7___ a.u. for the Cu and Zn complexes, respectively. A regular octahedron is stable for $[Zn(H_2O)_6]^{2+}$, and the calculated Zn-O bond length is 3.78 a.u. in agreement with the result of Clementi et al. (3.74 a.u.)[9] and slightly less than the experimental value (3.932 a.u.).[4] On the other hand, $[Cu(H_2O)_6]^{2+}$ showed two minima of the energy at the $(Cu\text{-}O)_z$ and $(Cu\text{-}O)_{x,y}$ bond lengths of 3.90(z) and 3.70(x,y) and of 3.667(z) and 3.817(x,y) a.u. No significant difference in energy was found between the two minima. The experimental bond lenghts[4] are 4.595(z) and 3.667(x,y), and their ratio is 1.25 which is much greater than the calculated value of 1.05. The calculated Jahn-Teller energy was 440 cm^{-1} which is about 1/5 of the experimental value. The smaller extent of Jahn-Teller distortion derived from the calculation may result from: (1) the neglect of solvent effect, (2) the limited basis set, and (3) the restricted Hartree-Fock formalism without configuration interactions. Additional calculations as described below did not affect the conclusion.

Calculations on the $(H_2O)_6$ cluster with the geometries of the stable $[Cu(H_2O)_6]^{2+}$ forms gave the total energies of -454.0149 (elongated) and -454.0149 a.u. (compressed), showing that the energies of ligand-ligand interactions are nearly identical in the two forms. Calculations were also made using a basis set with split d-functions; no significant difference in the total energy was found between the elongated and compressed complexes.

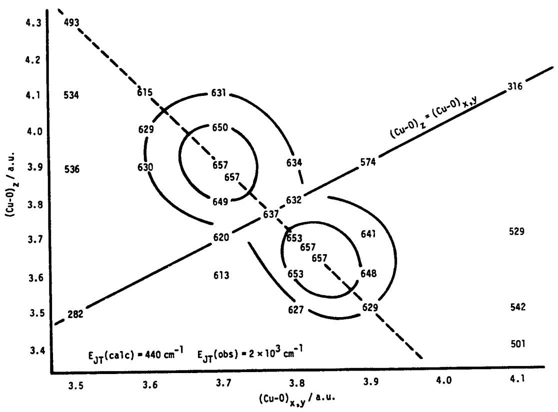

Fig. 1 $[Cu(H_2O)_6]^{2+}$ Potential Surface

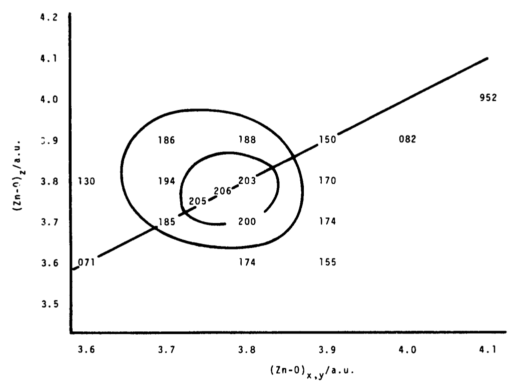

Fig. 2 $[Zn(H_2O)_6]^{2+}$ Potential Surface

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