JAHN–TELLER EFFECT IN HEXAHYDROXOCUPRATE(II) COMPLEXES

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Using semiempirical CNDO-UHF method the adiabatic potential surface of $^2[Cu(OH)_6]^{4-}$ complexes is investigated. The values of vibration and vibronic constants for $E_g - (a_{1g} + e_g)$ vibronic interaction attain extremal values for the optimal O–H distance. The Jahn–Teller distortion decreases with increasing O–H distance. The discrepancy between experimentally observed elongated bipyramid of $[Cu(OH)_6]^{4-}$ in $Ba_2[Cu(OH)_6]$ and the compressed one obtained by quantum-chemical calculation is explainable by hydrogen bonding of the axial hydroxyl group.

The Jahn–Teller effect represents an important conception frequently used in stereochemistry. The commonly accepted formulation of the Jahn–Teller theorem[1] states that a linear geometrical configuration of nuclei in an electronically degenerate state is unstable (except accidental and Kramers' degeneracy). Consequently, the system geometry is changed and the resulting stable configuration of nuclei corresponds to a lower symmetry group. However, the existence of such Jahn–Teller stable structures in solids is usually complicated by various solid state influence in real systems.

The crystal structure of $Ba_2[Cu(OH)_6]$, of the space group $P2_1/c$ (ref.[2]), contains highly distorted octahedrons of $[Cu(OH)_6]^{4-}$. These octahedrons do not share any edges or corners and appear to be held together primarily by barium ions. The highly distorted coordination octahedron of the cupric ion is formed by four equatorial ($d_{Cu-O(2)} = 1.972 \cdot 10^{-10}$ m and $d_{Cu-O(3)} = 1.958 \cdot 10^{-10}$ m) and two much more distant ($d_{Cu-O(1)} = 2.805 \cdot 10^{-10}$ m) axial oxygen atoms with practically perpendicular Cu–O bonds (the angle O(1)–Cu–O(2) is 93.1°, O(1)–Cu–O(3) 91.7°, and O(2)–Cu–O(3) 91.1°). This coordination is commonly referred as to 4 + 2 and is explained as being tetragonally distorted octahedral due to the Jahn–Teller effect of the double degenerate electronic E_g term. The considerable elongation of the axial bonds is ascribed to high negative charge of ligands[3].

The infrared spectrum of $Ba_2[Cu(OH)_6]$ consists of a sharp peak at 3 520 cm^{-1} indicating practically free OH group and a broader band at 3 320 cm^{-1} showing the presence of an OH group influenced by a weak hydrogen bond[2]. There is a single distance in the structure, $2.902 \cdot 10^{-10}$ m between O(1) and O(3), which is typical for hydrogen bonding. The coordination of O(1) including the hydrogen bonding to O(3) becomes approximately tetrahedral, O(1) being surrounded by three barium atoms and one oxygen atom. No definite hydrogen bonds seem to exist between O(1)–O(2) and O(2)–O(3) atoms[2]. The infrared spectral data indicate that the extremal elongation of the axial Cu–O(1) bond may be caused by O(1)–H(1)…O(3) hydrogen bonding. This may be the reason of axial O(1)–H(1) bond weakening. Alternative O(3)–H(3)…O(1) hydrogen bonding may not be excluded either. However, the too little difference between the Cu–O(2) and Cu–O(3) bond lengths makes it very improbable.

Our systematic study of characteristics of the adiabatic potential surface of Jahn–Teller octahedral complexes with doubly degenerate electronic E_g term has been restricted to halogen complexes of the first-row transition metals[4–6] and the solid state effects were approximated by point charges[7,8]. In hydroxo complexes, however, also the O–H bond strength may be modified by the solid state effects. The aim of this study is the quantitative investigation of the influence of O–H bond strength on the adiabatic potential surface of Jahn–Teller active systems. This may explain the relation between hydrogen bonding and Jahn–Teller distortion.

For the sake of comparability with our previous results[4–8], the semiempirical CNDO/2 method is used[9,10]. Our treatment cannot provide exact values of adiabatic potential surface parameters due to simplified model systems as well as due to approximations of the quantum chemical method used (ZDO treatment, semiempirical parametrization, valence basis set) but the observed trends in vibration and vibronic constants should be correct.

CALCULATIONS

Parameters of the adiabatic potential surface W for the $E_g - (a_{1g} + e_g)$ vibronic interaction in the O_h reference symmetry group may be very simply obtained when restricting to tetragonal distortions described by the changes of 2 axial (r_a) and 4 equatorial (r_e) Cu–O distances from the reference octahedral (r_0) one in the simple analytic form[5,6]

$$W(Q_a,Q_e) = K_aQ_a + \frac{1}{2}K_{aa}Q_a^2 + \frac{1}{2}K_{ee}Q_e^2 + T_aQ_a^3 + T_{ae}Q_aQ_e^2 - T_eQ_e^3 + \\ + s(A - ZQ_a)Q_e + sBQ_e^2 + E_0 \ , \qquad (1)$$

where K_a, K_{aa}, K_{ee}, T_a, T_{ae} and T_e are vibrational constants, A, B and Z are vibronic constants, Q_a and Q_e are symmetrized vibrational coordinates of a_{1g} and e_g ($x^2 - y^2$) symmetry, $s = +1$ for $r_a \geq r_e$ (elongated bipyramid) and $s = -1$ for $r_a < r_e$ (compressed bipyramid), and E_0 is the energy of the reference octahedron with the r_0 reference Cu–O distance.

In analogy with our previous papers[4–8], the symmetrized vibration coordinates may be used in the form

$$Q_a = \sqrt{\frac{2}{3}}\,(r_a + 2r_e - 3r_0)\ , \tag{2a}$$

$$Q_e = \sqrt{\frac{4}{3}}\,(r_a - r_e)\ . \tag{2b}$$

The values of vibronic and vibration constants of Eq. (*1*) may be determined by a least-squares fit.

RESULTS AND DISCUSSION

The vibration and vibronic constants were evaluated for $^2[Cu(OH)_6]^{4-}$ complexes with fixed O–H distances of 1.0 . 10^{-10} m, 1.068 . 10^{-10} m (optimum) and 1.1 . 10^{-10} m (see Table I). All Cu–O–H bond angles were fixed at 180° to comply with the reference O_h symmetry group. Moreover, such geometry corresponds to the lowest energy calculated

TABLE I

Calculated vibration and vibronic constant values of the systems under study for three fixed values of d_{O-H}. N is the number of points, ρ is the correlation coefficient. Units used: d_{O-H} and r_0 are in 10^{-10} m; A and K_a are in 10^{10} eV m^{-1}; B, Z, K_{aa} and K_{ee} are in 10^{20} eV m^{-2}; T_a, T_{ae} and T_e are in 10^{30} eV m^{-3}; 1 eV = 1.6022 . 10^{-19} J

Constant	Model		
	d_{O-H} = 1.0	d_{O-H} = 1.068	d_{O-H} = 1.1
N	33	53	39
r_0	1.89146	1.88587	1.88294
K_a	0.001	0.019	0.0001
K_{aa}	52.8	53.04	52.49
K_{ee}	38.49	36.4	38.69
T_a	–10	–12.3	–2
T_{ae}	–33	–30	–32
T_e	10.6	8	10
A	–0.9094	–0.788	–0.7905
B	0.39	0.36	0.44
Z	–1.3	–1.1	–1.2
ρ	0.999998	0.999992	0.999997

with valence basis sets and in the absence of external fields. The total molecular energy was calculated for selected geometries of the complex so that a two-dimensional numerical map of $W^c(Q_a,Q_e)$ was obtained. The standard semiempirical CNDO/2 method in UHF version for the transition metals[9] was applied for this purpose. The energy cut-off was 10^{-5} eV. The high reliability of our results of vibration and vibronic constants evaluation (presented by the number of significant digits in Table I) is indicated by high values of correlation coefficients. The extremal points (Q_a^e,Q_e^e) of adiabatic potential surfaces and the Jahn–Teller stabilization energies

$$E_{JT} = W(-K_a/K_{aa},0) - W(Q_a^e,Q_e^e) \qquad (3)$$

were determined from the calculated values of potential constants (see Table II).

Our results indicate many similarities with analogous hexahalocuprate(II) complexes[4]. The two-mode vibronic constant Z is higher than the quadratic vibronic constant B. The same relation holds for the vibration constants K_{aa} and K_{ee}. The values of

TABLE II

Extremal points of the adiabatic potential surface of the systems under study for three fixed values of d_{O-H}. Units used: d_{O-H}, Q_a^e, Q_e^e, r_a^e and r_e^e are in 10^{-10}; E_{JT} in 10^{-3} eV; 1 eV = 1.6022 . 10^{-19} J

Constant	Model		
	$d_{O-H} = 1.0$	$d_{O-H} = 1.068$	$d_{O-H} = 1.1$
	Minimum		
Q_a^e	–0.0003	–0.0054	–0.0002
Q_e^e	–0.0236	–0.0218	–0.0206
r_a^e	1.8777	1.8731	1.8710
r_e^e	1.8982	1.8919	1.8888
E_{JT}	10.82	8.62	8.17
	Saddle point		
Q_a^e	–0.0003	–0.0054	–0.0002
Q_e^e	0.0236	0.0215	0.0203
r_a^e	1.9050	1.8981	1.8946
r_e^e	1.8845	1.8794	1.8770
E_{JT}	10.66	8.44	7.97

harmonic vibration constants of our hydroxo complexes are greater than those for halo complexes whereas the reverse relation holds for the absolute value of the vibronic constant Z. The other constants (A, B, T_a, T_{ae}, T_e) are of comparable value both in hydroxo and halo complexes. In agreement with the trends observed previously[4], the lower r_0 values of hydroxo complexes correspond to larger distortion and higher Jahn–Teller stabilization energies E_{JT} than in halo complexes.

It is evident from our data in Table I that the maximum absolute values of K_a, K_{aa} and T_a vibration constants are observed for the optimum O–H distance ($1.068 \,.\, 10^{-10}$ m) whereas the absolute values of the other potential constants exhibit minimum values at this O–H distance. The values of r_0, r_a^e and r_e^e as well as the extent distortion (absolute value of Q_e^e) and E_{JT} decrease with the increasing O–H distance (see Table II). The energy barrier between minima (the energy difference between saddle points and minima) exhibit the opposite trend. Stable systems correspond to a compressed bipyramid regardless of the O–H distance.

CONCLUSIONS

The Jahn–Teller distortion decreases with the increasing O–H bond distance, i.e. with the decreasing O–H bond strength. Consequently, the decrease of O(1)–H(1) bond strength due to hydrogen bonding O(1)–H(1)…O(3) causes not only extra high elongation of the Cu–O(1) bond but also smaller Jahn–Teller effect. Discrepancy between the experimentally observed elongated bipyramid of $[Cu(OH)_6]^{4-}$ and the compressed one obtained by our quantum-chemical calculation is explainable by hydrogen bonding of the axial hydroxyl group. The calculated Jahn–Teller deformation is comparable with the observed difference between the Cu–O(2) and Cu–O(3) bond length. Comparison of axial and equatorial Cu–O bonds in $Ba_2[Cu(OH)_6]$ indicates that the energy of hydrogen bonding is much greater than the Jahn–Teller stabilization energy. Consequently, the $E_g – (a_{1g} + b_{1g} + b_{2g})$ vibronic coupling scheme within the D_{4h} symmetry group is appropriatte to describe the Jahn–Teller effect in $Ba_2[Cu(OH)_6]$.

Finally, it must be mentioned that our proposed relations for Cu–O bond lengths in $Ba_2[Cu(OH)_6]$ represents only one of possible explanations of the experimental data. Solid state effects in real systems may cause relevant changes in bond lengths and angles. In order to verify our conclusions, the use of more complex model systems as well as of more sophisticated quantum-chemical methods is desirable.

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