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Density Functional Calculations on the Geometries and Dissociation Energies of $[M(H_2O)_6]^{2+}$ Ions.
$M^{2+} = Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$, and Zn^{2+}

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Full geometry optimizations have been carried out on high-spin hexaaqua complexes of Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} by the local spin density functional method with non-local corrections using Gaussian-type basis sets. The octahedral molecular arrangement around the Mn^{2+}, Ni^{2+}, and Zn^{2+} ions optimized were regular, whereas those around the Cr^{2+}, Fe^{2+}, Co^{2+}, and Cu^{2+} ions were distorted with significant differences in the three kinds of M-O distances. The Jahn-Teller distortion for the Fe^{2+} and Co^{2+} complexes was firstly found in the field of computational geometry optimization.

The accurate theoretical treatment of hydrated complexes of high-spin divalent transition-metal ions has long been a subject of interest for solution and coordination chemists. The metal-water distances in the hydrated ions in solution have been investigated by the X-ray diffraction, neutron diffraction and EXAFS methods.1-3) In the case of the hydrated Cu^{2+} complexes, the structure has been found to be an tetragonally elongated octahedron undergoing Jahn-Teller distortion.1-3) With a view to elucidate it, theoretical calculations on the metal-water distances and/or the dissociation energies have been carried out for the axially distorted octahedral hexaaqua complexes of Cr^{2+} and Cu^{2+} and the regular octahedral complexes of the hexaaqua Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} ions.2,4-7) The Jahn-Teller theorem, however, lets us also expect a distorted structure of the Fe^{2+} and Co^{2+} complexes. The density functional theory recently developed8,9) makes possible accurate calculations of energies and gradient geometry optimization, which is computationally efficient and useful for the precise studies of structures of the hexaaqua complex of transition metal ions. In this paper, we report results of the ab initio calculations on the metal-water bond distances and the hydration energies of the hexaaqua complexes of high-spin divalent transition metal ions by the density functional method.

Ab initio calculations were carried out according to the density functional scheme by the use of DGauss program,8,9) which can perform calculations on isolated molecules using the local spin density variant of density functional. The basis sets are Gaussian functions; (12s9p5d)/[5s3p2d] for transition metals, (9s5p1d)/[3s2p1d] for oxygen atom and (5s)/[2s] for hydrogen atom.8,9) The transition metals were assumed to be in the high-spin state. Exchange and correlation energies were included in the non-local corrections developed by Becke10) and

Perdew[11] with about 42000 grid points. The error in the calculation of the total energies is less than 1×10^{-4} a.u. The initial value of the M-O distance was 206.0 pm for all metal ions and water molecules were placed at the apexes of a regular octahedron with T_h symmetry around a metal atom. The structure of a water molecule was assumed to have the O-H bond length of 95.0 pm and the H-O-H angle of 105.0°. No symmetrical rstriction was used during the calculation. All calculations were performed by CRAY Y-MP8I/8128 computer.

The bond parameters and dissociation energies optimized for $[M(H_2O)_6]^{2+}$ are summarized in Table 1, together with previous results experimentally obtained[12] as well as those calculated.[2,5,6] All the O-M-O angles in the optimized complexes showed 90° and 180° within ±0.1°. As is obvious from Table 1 and Fig. 1, the most interesting fact found in this study is that the Jahn-Teller distortion is found not only for the Cr^{2+} and Cu^{2+}

Table 1. Calculated M-O Distances, H-O-H Angles and Binding Energies

	M-O Distance/pm					Hydration Energy/kJ mol^{-1}			
	Calcd. [H-O-H angle/°]	Exp.[a] (solution)	Exp.[b] (Tutton salt)	Calcd.[h] (HF)	Calcd.[i] (CNDO)	Calcd.	Exp.[j]	Calcd.[h] (HF)	Calcd.[l] (ES)
Cr	202.5(x2)[109.1]			213(x4)	211(x4)	1453	1925	1529	
	202.8(x2)[108.5]			232(x2)	222(x2)				
	226.8(x2)[106.1]								
Mn	212.1(x6)[107.4]	219.2(x6)	215(x2)[c]	219(x6)	207(x6)	1366	1920	1510	1288
			219(x2)						
			220(x2)						
Fe	207.0(x2)[108.1]	211.4(x6)	208.6(x2)[d]	214(x6)	203(x6)	1491	2008	1577	1398
	207.2(x2)[108.0]		213.6(x2)						
	207.5(x2)[108.1]		215.6(x2)						
Co	202.8(x2)[108.9]	210.6(x6)	207.0(x2)[d]	209(x6)	194(x6)	1626	2105	(1588)[k]	1456
	203.8(x2)[108.7]		210.6(x2)						
	205.6(x2)[108.3]		210.7(x2)						
Ni	200.2(x6)[109.7]	206.1(x6)	203.9(x2)[e]	205(x6)	188(x6)	1705	2170	1689	1524
			207.2(x2)						
			207.3(x2)						
Cu	197.3(x2)[109.3]	196.8(x4)	196.6(x2)[f]	200(x4)	186(x4)	1624	2174	1710	1534
	199.0(x2)[107.5]	240 (x2)	207.3(x2)	212(x2)	195(x2)				
	219.3(x2)[106.1]		223.0(x2)						
Zn	205.7(x6)[108.5]	209.8(x6)	207.5(x2)[g]	204(x6)		1514	2120	1688	1456
			211.7(x2)						
			212.9(x2)						

a) M-O distances in solution. Data from Ref. 3. b) M-O distances in Tutton salts of ammonium transition metal(II) sulfate hexahydrate. c) Data for Ref. 13. d) Data from Ref. 14. e) Data from Ref. 15. f) Data from Ref. 16. g) Data from Ref. 17. h) Hartree-Fock method. Data from Ref. 6. i) CNDO method. Data from Ref. 5. j) Data from Ref. 12. k) The value quoted here may not be the self-consistent energy. l) Electrostatic model. Data from Ref. 2.

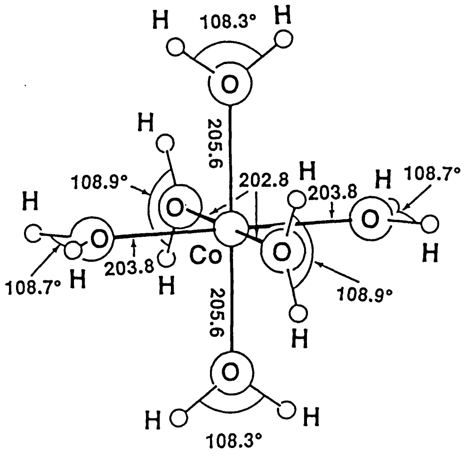

Fig. 1. Optimized geometry of $[Co(H_2O)_6]^{2+}$ complexes. Distances are in the unit of pm.

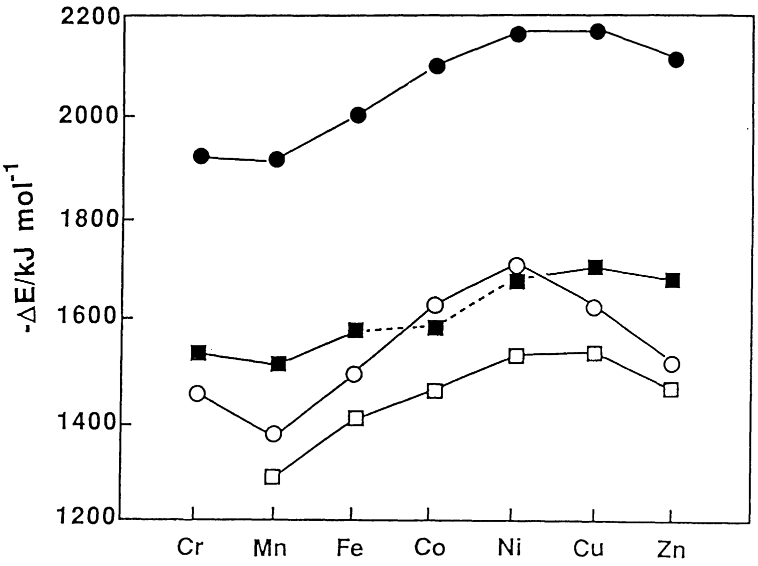

Fig. 2. Calculated dissociation energies and experimental hydration energy of $[M(H_2O)_6]^{2+}$ complexes. Open circles, open squares, and closed squares are calculated values in this work, Ref. 2., and Ref. 6, respectively. Closed circles are experimental values from Ref. 12.

complexes but for the Fe^{2+} and Co^{2+} complexes. That is, the octahedral structure of the hexaaqua Cr^{2+}, Fe^{2+}, Co^{2+}, and Cu^{2+} ions are distorted, while the octahedra of the hexaaqua complexes of Mn^{2+}, Ni^{2+}, and Zn^{2+} ions are regular where the M-O distances of each complex are the same within ±0.1 pm. The degree of distortion is in good agreement with those expected from the Jahn-Teller effect[18)] (Cr^{2+}, $Cu^{2+} > Fe^{2+}$, Co^{2+}); i. e., the octahedral structure of the hexaaqua complexes are strongly distorted for Cr^{2+} and Cu^{2+}, slightly distorted for Fe^{2+} and Co^{2+}, and regular for Mn^{2+}, Ni^{2+}, and Zn^{2+}. According to Beagly et al.[7)] who investigated on the distortion of T_h symmetry in the $[Cu(H_2O)_6]^{2+}$ complex by ab initio SCF molecular orbital calculations, the four equatorial Cu-O distances were kept to be equal during the calculations. Our results clearly show that the hexaaqua complexes of the so-called Jahn-Teller ions exhibit a slightly distorted rhombic structure, i. e., the M-O distances on the equatorial plane are grouped into two as shown in Fig. 1 and Table 1.

The M-O distances optimized seem to be shorter than those experimentally determined in solution, although the general trend of the M-O distances in the $[M(H_2O)_6]^{2+}$ complexes coincides with the experimental values. The long M-O distances in solution may be due to the interaction between the coordinated water molecules and water molecules in the outer sphere. The optimized geometry of a water molecule has the O-H distance of 97.7 pm, H-O-H angle of 105.7°, and the total energy of -76.4424 a.u. The H-O-H angle in the $[M(H_2O)_6]^{2+}$ complexes optimized seems to increase with decreasing M-O distance, although the O-H distances for all water molecules are nearly equal (98.5±0.1 pm). The variation of the H-O-H angle may be attributed to the effect of partial acceptance of lone-pair electrons of water by the transition-metal $d\pi$-orbitals as described by Sano and Yamatera.[6)] The dissociation energy is expressed as the difference between the total energy of the hexaaqua ion and the sum of energies of the corresponding metal ion and six water molecules singly optimized. The energies show a trend similar to the hydration energies experimentally determined[12)] as shown in Fig. 2. Previous results obtained by the traditional molecular orbital calculations[6)] and by using the simple electrostatic model[2)] are also similar to ours, although the convexity of the curves is slightly smaller than ours. The difference between the experimental hydration enthalpies and the calculated energies is due to the neglect of the second and further hydration spheres in the theoretical calculations.[4a,4b,4e,6)]

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