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Application of Density Functional Calculations to the Structures and Formation Energies of $[MCl_4]^{2-}$ Complexes (M=Cr, Mn, Fe, Co, Ni, Zn)[#]

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The structures and the formation energies of $[MCl_4]^{2-}$ (M=Cr, Mn, Fe, Co, Ni, Zn) have been examined by the density functional method. The optimized structures of $[MnCl_4]^{2-}$, $[CoCl_4]^{2-}$ and $[ZnCl_4]^{2-}$ are a regular tetrahedron with the M–Cl distances of 236, 227, and 231 pm, respectively. The structures of $[CrCl_4]^{2-}$ and $[FeCl_4]^{2-}$ are a flattened tetrahedron with the M–Cl distances of 236 and 231 pm, respectively, and with the flattening angles of 156 and 112°, respectively, while that of $[NiCl_4]^{2-}$ is a tetrahedron elongated along an S_4 axis with the Ni–Cl distance of 226 pm and the corresponding angle of 97°. The formation energies of $[MCl_4]^{2-}$ have been compared with their experimental data, and the relative energies of the transformation from $[M(H_2O)_6]^{2+}$ to $[MCl_4]^{2-}$ are also evaluated in connection with the stability of the anions in aqueous solutions.

The density functional method is the ab initio method logically situated in the same level as the Hartree–Fock method, in which a total energy of chemical system is expressed as a functional of charge density without any empirical or adjustable parameters on the basis of the many-body theory.[1)] Recently, the density functional method with Gaussian basis sets have been developed and made possible the accurate calculation of energy and geometry optimization even for weak interaction such as hydrogen bond at the same level as the Møller–Plesset second perturbation methods (MP2).[2)] This method is computationally efficient and reliable, and thus it is very convenient for the study of large chemical systems.

Transition metal (II) tetrachloro complexes are one of the most popular polyatomic anions, which form tetrahedral or square-planar configulations. According to the ligand field theory, the set of d orbitals in a regular tetrahedral field splits into a doublet e orbital (d_{z^2}, $d_{x^2-y^2}$) and a triplet t_2 orbital (d_{xy}, d_{xz}, d_{yz}).[3)] The Jahn–Teller effect predicts that the most stable configurations of the tetrahedral complexes of Cr^{2+} (d^4), Fe^{2+} (d^6), Ni^{2+} (d^8) and Cu^{2+} (d^9) in high spin state are distorted tetrahedra.[3)] In the case of Cr^{2+} or Cu^{2+}, the tetrahedral complexes should be led to a flattened tetrahedron, in which the d_{xy} orbital is destabilized and the d_{xy} and d_{yz} orbitals are stabilized.[3)] On the other hand, in the case of Ni^{2+}, the tetrahedron will be elongated along an S_4 axis, in which just the reverse splitting of t_2 orbital occurs, i. e. the singlet d_{xy} orbital is stabilized and the d_{xz}, d_{yz} doublet is destabilized.[3)] The Jahn–Teller effect, however, offers no quantitative information about the distortions and about whether the more stable configuration for tetrahedral complex of Fe^{2+} is the flattened or the elongated tetrahedron.[3)]

In the previous work, we were examined the structures of $[M(H_2O)_6]^{2+}$ (M=Cr, Mn, Fe, Co, Ni, Cu, Zn) by the density functional method, in which the formation energies of $[M(H_2O)_6]^{2+}$ in isolated states were determined on the basis of Eq. 1.[4)]

$$M^{2+} + 6H_2O \rightarrow [M(H_2O)_6]^{2+}. \qquad (1)$$

Recently, we also performed full geometry optimizations of $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ by the same method, and found that the most stable structures are flattened tetrahedra as predicted by the Jahn–Teller effect and the structures are in very good agreement with those experimentally established.[5)] No systematic theoretical calculations for a series of $[MCl_4]^{2-}$ complexes, however, have been performed to obtain their structures and the formation energies, although the electronic structures of the anions have been repeatedly investigated by many theoretical methods.[3,6)]

In the present work, the full geometry optimizations have been carried out to obtain the stable structures for a series of tetrachloro transition metal (II) complexes of $[MCl_4]^{2-}$ (M=Cr, Mn, Fe, Co, Ni, Zn) by the density functional method and their formation energies in isolated states have been calculated according to Eq. 2.

$$M^{2+} + 4Cl^- \rightarrow [MCl_4]^{2-}, \qquad (2)$$

which have been compared with those obtained experimentally. Using the previous[4,5)] and present results, the energies of the transformation of $[M(H_2O)_6]^{2+}$ to $[MCl_4]^{2-}$ in isolated states as expressed by Eq. 3,

$$[M(H_2O)_6]^{2+} + 4Cl^- \rightarrow [MCl_4]^{2-} + 6H_2O \qquad (3)$$

have been also calculated, and briefly discussed in connection with the stability of the salts in aqueous solutions.

[#] This paper is dedicated to the late Professor Hiroshi Kato.

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Calculation Details

The ab initio calculations were carried out according to the density functional scheme by the use of DGauss program.[2] The following Gaussian-type basis sets were used; (63321/531/41) and (6321/521/1) for transition metals and chlorine with the uncontracted auxiliary basis sets of (10/5/5) and (9/4/4), respectively. The transition metals were assumed to be in a high-spin state. Geometry optimizations have been self-consistently performed within the local spin density (LSD) approximation. After that, nonlocal corrections proposed by Becke[7] and Perdew[8] for the exchange and correlation interactions have been applied, which can improve the energies of LSD approximation to the similar level as the MP2 method. The SCF convergence thresholds for the density and total energies are at 5×10^{-5} and 5×10^{-7} a. u., respectively. The convergence criterion for the largest gradient component is at 8×10^{-4} a. u.

In the calculations, the Cl^- ions were initially located within T_d symmetry around a metal atom with the M–Cl distance of 220.0 pm for all metal ions. No symmetrical restriction was used during the calculation.

All calculations were performed by CRAY Y-MP supercomputers.

Results and Discussion

Optimized Structures. The optimized structures of $[MCl_4]^{2-}$ are illustrated in Fig. 1, which are nearly regular or tetragonally distorted tetrahedra. The M–Cl distances and the equivalent Cl–M–Cl angles in each complex are equal within ±1 pm and ±1°, respectively, although the geometries of the complexes have been fully optimized.

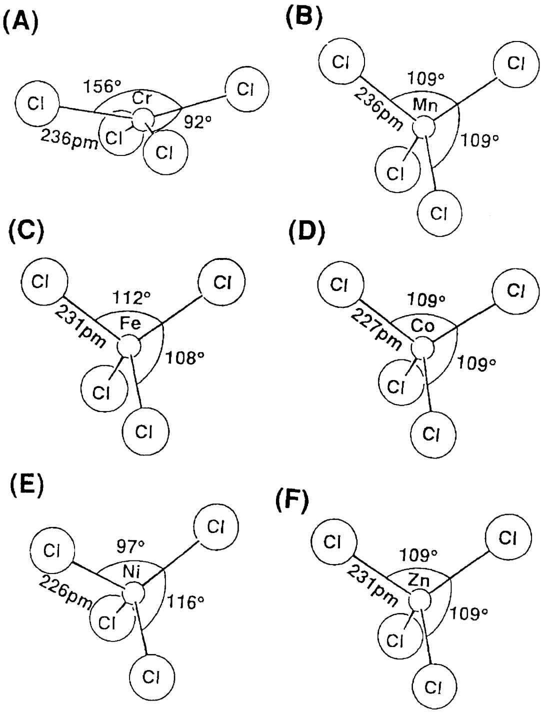

Fig. 1. Optimized structures of $[MCl_4]^{2-}$.

The structure of $[CrCl_4]^{2-}$ (Fig. 1(A)) was a flattened tetrahedron with the Cr–Cl distance of 236 pm and the Cl–Cr–Cl flattening angle of 156°. Those of $[MnCl_4]^{2-}$ (Fig. 1(B)), $[CoCl_4]^{2-}$ (Fig. 1(D)), and $[ZnCl_4]^{2-}$ (Fig. 1(F)) were regular tetrahedra with the M–Cl distances of 236, 227, and 231 pm, respectively. The optimization of $[FeCl_4]^{2-}$ complex converged to a flattened tetrahedron with the Fe–Cl distance of 231 pm and the flattening angle of 112°. The structure of $[NiCl_4]^{2-}$ is a tetrahedron elongated along an S_4 axis with the Ni–Cl distance of 226 pm and the corresponding angle smaller than 109°.

The M–Cl distances optimized here are in good agreement with those experimentally determined except for $[CrCl_4]^{2-}$ whose structure has not been reported; 235 pm for Mn,[9] 231 pm for Fe,[10] 227 pm for Co,[11] 226 pm for Ni,[11a] and 227 pm for Zn.[12]

The $[MCl_4]^{2-}$ anions in the real crystals are irregularly distorted and the Cl–M–Cl angles are dispersed within the range of 105—112° for Mn,[8] 103—121° for Fe,[9] 97—112 for Co,[10] 103—114° for Ni,[10a] and 102—120 for Zn.[11] The slight deviations between the optimized and experimental values may be attributable to the so-called crystal environments such as hydrogen bonding and crystal packing.

Energies. The total energies of $[MCl_4]^{2-}$ are summarized in Table 1 together with those of $[M(H_2O)_6]^{2+}$ calculated previously.[5] The energies of the left and right sides of the Eq. 3, (A) and (B), respectively, and the differences between them, ΔE_M, are also listed in Table 1. The energies of (B) are lower than the energies of (A) for the respective transition metal.

The formation energies of $[MCl_4]^{2-}$ (Eq. 2) are sum-

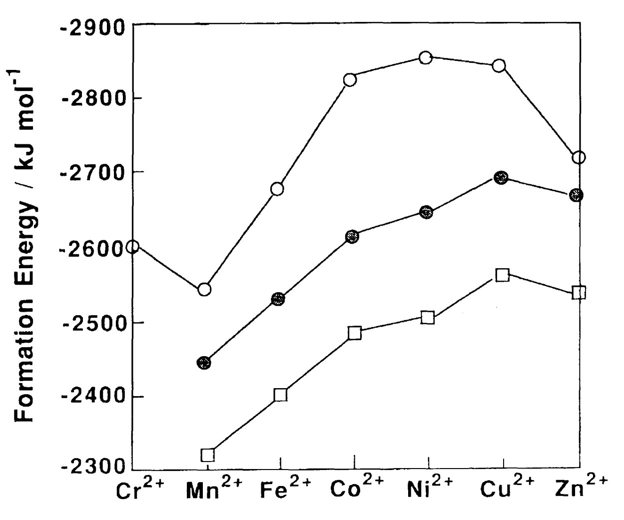

Fig. 2. Formation Energies of $[MCl_4]^{2-}$. Open circles are those calculated in this work. Open squares and closed circles are experimental values evaluated from Ref. 13 and Refs. 15 and 16, respectively.

Table 1. Comparison of Total Energies of $[MCl_4]^{2-}$ and $[M(H_2O)_6]^{2+}$ Complexes (a. u.)

M	$[M(H_2O)_6]^{2+}$,a)	$[MCl_4]^{2-}$,b)	$[M(H_2O)_6]^{2+}$ $+4Cl^{-}$,c) (A)	$[MCl_4]^{2-}$ $+6H_2O$ d) (B)	ΔE_M e) (B)−(A)
Cr	−1502.708018	−2885.568210	−3343.783882	−3344.222670	−0.438788(−1153)
Mn	−1609.244591	−2992.115251	−3450.320455	−3450.769711	−0.449256(−1180)
Fe	−1721.921765	−3104.794940	−3562.997629	−3563.449400	−0.451771(−1185)
Co	−1840.967178	−3223.846758	−3682.043042	−3682.501218	−0.458176(−1203)
Ni	−1966.496425	−3349.357339	−3807.572289	−3808.011799	−0.439510(−1155)
Cu	−2098.603362	−3481.491165	−3939.679226	−3940.145625	−0.466399(−1224)
Zn	−2237.540837	−3620.421944	−4078.616701	−4079.076404	−0.459703(−1208)

a) Taken from Ref. 4. b) This work. The value for $[CuCl_4]^{2-}$ is taken from Ref. 5. c) The value of −460.268966 a. u. was used as the energy of the Cl^- ion, which was evaluated by the same method as performed here. d) The total energy for a water molecule, −76.442410 a. u., was taken from Ref. 4. d) The number in parenthesis is expressed as $kJ\,mol^{-1}$ unit.

Table 2. Comparison of Formation Energies of $[MCl_4]^{2-}$ and $[M(H_2O)_6]^{2+}$ Complexes ($kJ\,mol^{-1}$)

	$[MCl_4]^{2-}$			$[M(H_2O)_6]^{2+}$	
	Calcd a)	Exp. 1 b)	Exp. 2 c)	Calcd d)	Exp. e)
Cr	−2606	—	—	−1453	−1925
Mn	−2546	−2315	−2447	−1366	−1920
Fe	−2677	−2404	−2532	−1491	−2008
Co	−2828	−2489	−2617	−1626	−2105
Ni	−2859	−2507	−2650	−1705	−2170
Cu	−2848	−2566	−2692	−1624	−2174
Zn	−2721	−2542	−2669	−1514	−2120

a) This work. The value for $[CuCl_4]^{2-}$ is taken from Ref. 5. b) The values were evaluated from the absolute formation energy for $[ZnCl_4]^{2-}$ (−2542 $kJ\,mol^{-1}$, Ref. 13) and the reletive formation energies among $[MCl_4]^{2-}$ complexes (Ref. 13), as described in the Results and Discussion. c) The values were obtained as the sum of the absolute formation energy calculated for $[ZnCl_4]^{2-}$ (−2669 $kJ\,mol^{-1}$, Ref. 15) by using the analytical models and the relative energies determined experimentally for that (Ref. 16). c) Taken from Ref. 4. e) Taken from Ref. 17.

marized in Table 2 and Fig. 2 together with those estimated experimentally by two different ways. One, Exp. 1 in Table 2, was obtained by using the results reported by Paoletti and Vacca;13) the formation energy of −2542 $kJ\,mol^{-1}$ for $[ZnCl_4]^{2-}$ was estimated by using the modified Kapunstinskii's formula14) and those for other $[MCl_4]^{2-}$ complexes were calculated from the relative formation energies determined by the measurements of the heat of dissolution of $[(NMe_4)_2MCl_4]$ (NMe_4; tetramethylammonium).12) Another, Exp. 2 in Table 2, was calculated from the values proposed by Blake and Cotton;15,16) the absolute formation energy of $[ZnCl_4]^{2-}$ was estimated to be −2669 $kJ\,mol^{-1}$ by using the pseudo-lattice energies calculated by their analytical models,15) and those for other $[MCl_4]^{2-}$ complexes were obtained from the relative formation energies among $[MCl_4]^{2-}$ determined from the thermodynamic data of $[(C_6H_5)_3CH_3As]_2MCl_4$.15) The formation energies of $[MCl_4]^{2-}$ optimized here are larger than both of the experimental values, although the hydration energies calculated previously4) have been smaller than those determined experimentally.17) The differences in $[M(H_2O)_6]^{2+}$ were explained by the effect of the outer hydration spheres in the real solutions.4) Those in $[MCl_4]^{2-}$ may be due to the effects of environments around the complexes in the crystalline state; e.g. the $[MCl_4]^{2-}$ complexes in the crystalline states do not necessarily form the most stable configurations on account of the crystalline environments such as hydrogen bonding and crystal packing as described above, and thus the formation energies of the somewhat unstable structures may be estimated to be lower than those of the most stable ones calculated here.

The stabilities for $[MCl_4]^{2-}$ complexes in aqueous solutions have been estimated as differences between ΔE_M for a particular metal complexes and ΔE_{Co} for Co^{2+} complex in Eq. 3 ($\Delta E_M - \Delta E_{Co}$), which are listed in Table 3 together with the relative experimental values reported hitherto.13,15,17) The relative stabilities for the Co^{2+} and Ni^{2+} complexes calculated here is in agreement with the experimental ones, although the stabilities among other complexes are not in so good agreement with those obtained experimentally. It is well coincident with the facts that $[CoCl_4]^{2-}$ is relatively stable in aqueous solutions but $[NiCl_4]^{2-}$ is not so stable,

Table 3. Comparison of Differences between ΔE_M and ΔE_{Co} in Eq. 3 ($kJ\,mol^{-1}$)

	Cr	Mn	Fe	Co	Ni	Cu	Zn
Calcd a)	50	23	18	0	48	−21 b)	−5
Exp. c)	—	−11	−12	0	47	8	−38
Exp. d)	—	−2	8	0	44	−12	—
Exp. d)	—	−10	14	0	47	8	−35
Exp. e)	—	0	4	0	75	33	−25

a) This work. b) Taken from Ref. 5. c) Taken from Ref. 13 and Ref. 17. d) Derived from some thermodynamic cycles in Ref. 15. e) Determined from the differences between the crystal field stabilization energies estimated in some complexes (Ref. 15).

as described elsewhere.[16,18]

As described in this work, the density functional calculation with Gaussian-type basis sets, which has been developed recently, is available for all atoms and has been shown to give structural and energetic informations even for relatively large chemical systems such as the transition metal complexes.

A part of the calculations was carried out at the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University.

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