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Intrinsic Structures of $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ Anions by Ab Initio Density Functional Calculations

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The intrinsic structures of $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ have been investigated by ab initio density functional method and determined to be D_{2d} symmetry with the flattening X-Cu-X angles of 138° and 130° for the case of X = Cl and Br, respectively, and the Cu-X distances of 228 pm and 241 pm, respectively, which are good agreement with the experimental data.

The structures of $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ anions in crystalline state are one of the most attractively and intensively studied transition metal complex anions. It has been described that these anions usually exist as a flattened tetrahedron with approximately D_{2d} symmetry due to the Jahn-Teller distortions; the two flattening angles, θ(X-Cu-X) (X = Cl, Br), are larger than the regular tetrahedral angle (109.5°) and the other four are smaller than that. Structural data for 66 $[CuCl_4]^{2-}$ and 15 $[CuBr_4]^{2-}$ anions reported hitherto, however, seem to be somewhat different.[1-7] In the case of $[CuCl_4]^{2-}$, the ranges of θ are classified into three types; 105.2° - 115.0° (av. 110°) for 3 species with nearly T_d symmetry, 125.6° - 159.3° (av. 136°) for 57 species with nearly D_{2d} symmetry, and 178.5°-180.0° (av. 180°) for 6 species with nearly D_{4h} symmetry.[1-4] On the other hand, those in $[CuBr_4]^{2-}$ anion distribute only in the range of 118.9° - 142.1° (av. 130°) for 15 species with nearly D_{2d} symmetry, which is smaller than that of $[CuCl_4]^{2-}$.[5-7]

Geometry optimizations of $[CuCl_4]^{2-}$ anion have been previously carried out with the restriction of D_{2d} conformation by ab initio Hartree-Fock (HF) method.[8] The optimized θ angles (115° - 120°), however, were smaller by about 20° than the average of those for 57 $[CuCl_4]^{2-}$ anions with D_{2d} symmetry (136°), and the optimized Cu-Cl distances, 237-247 pm, were also longer by about 13-23 pm than the average value for the 57 anions (224 pm). For $[CuBr_4]^{2-}$, such a calculation has not been performed yet, because the anion is too big to try the full geometry optimization by ab initio HF method. Thus, the theoretical treatment for intrinsic structures of their anions were waited.

The density functional theory recently developed made it possible to carry out the accurate calculations of energies and gradient geometry optimizations to relatively large chemical systems with relatively low computational expense at the same level as the Møller-Plesset second order perturbation method (MP2).[9-12] We report here the intrinsic structures of the $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ anions as studied by ab initio density

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functional calculations.

Ab initio calculations were carried out according to the density functional scheme by the use of DGauss program.[9-11] The Gaussian-type basis sets were used at the double-zeta-split-valence plus polarization (DZVP) level; (63321/531/41) for copper, (63321/5321/41) for bromine and (6321/521/1) for chlorine, with the unconstructed auxiliary basis sets of (10/5/5), (10/5/5) and (9/4/4), respectively.[9,10] Geometry optimizations have been self-consistently performed within the local spin density (LSD) approximation. After that, nonlocal corrections proposed by Becke[13,14] and Perdew[15] for the exchange and correlation interactions have been applied, which can improve the results by LDS approximation to the similar level to the MP2 method. The SCF convergence thresholds for the density and total energies are at 5×10^{-5} a.u. and 5×10^{-7} a.u., respectively. The convergence criterion for the largest gradient component is at 8×10^{-4} a.u. All calculations were performed on CRAY Y-MP supercomputers.

The geometry optimizations were carried out for the following three cases; the two were optimized on the Cu-X distances for the anions restricted to T_d or D_{4h} symmetries and another was fully optimized from T_d symmetry as starting geometry without any symmetrical restriction. In all cases, the initial Cu-Cl and Cu-Br distances were assumed to be 240 pm and 250 pm, respectively.

The full geometry-optimized structures for $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ without any restriction, as started from T_d symmetry, are shown in Fig. 1(A) and (D), respectively. The structures for $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ anions optimized with the restriction of T_d symmetry are shown in Fig. 1(B) and (E), respectively. Those for the anions with the restriction of D_{4h} symmetry are shown in Fig.1(C) and (F), respectively. The comparison of the total and dissociation energies is given in Table 1. The structures of $[CuX_4]^{2-}$ anions fully optimized from T_d symmetry were both converged to the flattened tetrahedra (D_{2d} symmetry), with the flattening angles of 138° and 130° for $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ anions, respectively, which are in good agreement with the average of the angles previously examined, 136° and 130°, respectively.[1-7] The Cu-Cl (228 pm) and Cu-Br (241 pm) distances obtained here are also close to the averages of 57 $[CuCl_4]^{2-}$ and 15 $[CuBr_4]^{2-}$ anions with the D_{2d} structure estimated experimentally, 224 and 238 pm, respectively.[1-7]

The Cu-X distances in the structures optimized with the restriction of T_d symmetry, 228 and 241 pm for $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$, respectively, were quite the same with those fully optimized, within calculation error. On the other hand, those optimized with the restriction of D_{4h} symmetry, 230 pm and 245 pm for $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$, respectively, were slightly elongated in comparison with those of the D_{2d} and T_d structures. Although there is no experimental report on the $[CuBr_4]^{2-}$ anion with T_d or D_{4h} symmetries, such a tendency is seen also in the Cu-Cl distance for $[CuCl_4]^{2-}$ anions; the average values are 224 pm for 57 (D_{2d}) and 3 (T_d) $[CuCl_4]^{2-}$ anions, and 226 pm for 6 (D_{4h}) anions.[1] The elongation of the Cu-X distances in the D_{4h} structure should be attributable to the steric repulsion between the neighboring halogen ions.

As shown in the comparison of the dissociation energies in Table 1, the $[CuCl_4]^{2-}$ anion is more stable in the T_d and D_{4h} structures by 7.0 kJ mol^{-1} and 7.3 kJ mol^{-1}, respectively, than the D_{2d} structure. In the case of $[CuBr_4]^{2-}$ anion, the D_{2d} structure is also more stable by 13.4 kJ mol^{-1} and 28.6 kJ mol^{-1}, respectively, than the T_d and D_{4h} structures. The differences between the energies of the T_d or D_{4h} structures and the most stable D_{2d} structure for $[CuBr_4]^{2-}$ are larger than those of $[CuCl_4]^{2-}$. The relative energies should be reflected to the distribution in the structures of the anions, e. g. no $[CuBr_4]^{2-}$ anions with D_{4h} symmetry are found in crystal, while those of $[CuCl_4]^{2-}$ are formed in some crystals.[1-7] The deviation from the most stable D_{2d} geometry should be ascribed to effects from crystalline environments such as hydrogen bond and electrostatic force.

Table 1. Comparison of energies computed for the $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ anions which were optimized with T_d, D_{2d} and D_{4h} symmetries

Anion	Geometry	Total energy /a.u.	Dissociation energy /kJ mol^{-1}	Relative energy a) /kJ mol^{-1}
$[CuCl_4]^{2-}$	(A) D_{2d}	-3481.49118	-2848.3	0
	(B) T_d	-3481.48849	-2841.3	7.0
	(C) D_{4h}	-3481.48840	-2841.0	7.3
$[CuBr_4]^{2-}$	(D) D_{2d}	-11936.66853	-2920.1	0
	(E) T_d	-11936.66343	-2906.7	13.4
	(F) D_{4h}	-11936.65764	-2891.5	28.6

a)Difference between the dissociation energies, E, of the T_d or D_{4h} structures and the most stable D_{2d} structure ($E(T_d$ or $D_{4h}) - E(D_{2d})$).

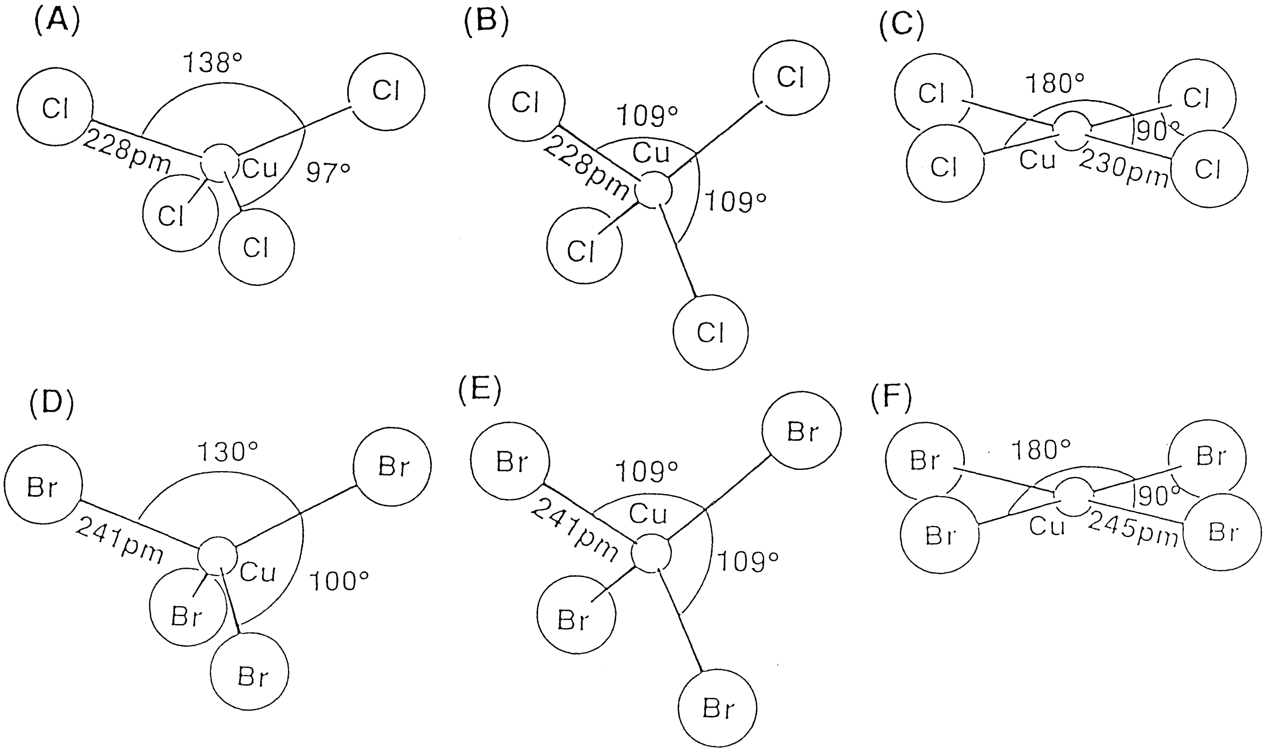

Fig.1. Optimized geometries of $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ anions. (A) and (D) are the most stable structures (D_{2d}) obtained by full geometry optimizations, (B) and (E) show the structures optimized with restriction of T_d symmetry, and (C) and (F) are those optimized within D_{4h} configuration.

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