Formation of $[CoCl_4(H_2O)_2]^{2-}$ complex in $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$ double salt: structural and energetic properties of $[MCl_4(H_2O)_2]^{2-}$ and $[M(H_2O)_6]^{2+}$ $(M = Mg, Co)$

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Abstract

The crystal structure of the double salt $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$ has been determined by the X-ray diffraction method. It crystallizes in the space group $P\bar{1}$ with $a = 6.0976(9)$, $b = 6.308(1)$, $c = 8.579(3)$ Å, $\alpha = 81.99(2)°$, $\beta = 88.40°$, $\gamma = 84.61(1)°$, $Z = 1$, and $R = 0.027$. The crystal consists of two kinds of well separated octahedra, $[CoCl_4(H_2O)_2]^{2-}$ and $[Mg(H_2O)_6]^{2+}$. The former is unique as aquachloro complexes of Co^{2+}. In order to elucidate the reason prepared as such unique complexes in the double salts, formation energies for $[MCl_4(H_2O)_2]^{2-}$ and $[M(H_2O)_6]^{2+}$ $(M = Co, Mg)$ have been calculated by using the density functional methods, and it has been revealed that the formation energies of the first coordination sphere for the metal ions and the $Cl^- \cdots H_2O$ hydrogen bond networks around $[CoCl_4(H_2O)_2]^{2-}$ play a decisive role in forming $[CoCl_4(H_2O)_2]^{2-}$ with the regular octahedral geometry in the double salt.

Keywords: Double salts; Crystal structures; Cobalt complexes; Magnesium complexes

1. Introduction

The tetrachloro cobalt(II) complexes reported hitherto are usually tetrahedral $[CoCl_4]^{2-}$ complex not only in solution but also in solid states. The diaquatetrachloro cobalt(II) complex, $[CoCl_4(H_2O)_2]^{2-}$, was recently determined as a component in $2RbCl \cdot CoCl_2 \cdot 2H_2O$ double salt by the single crystal X-ray diffraction methods [1]. In our knowledge, it was the only verified three-dimensional structure of the tetrachloro cobalt(II) complex with an octahedral geometry by the methods, although existence of $[CoCl_4(H_2O)_2]^{2-}$ has been frequently predicted and discussed in some double salt crystals [2–6].

Previously the complex formation in double salt crystals was quantitatively discussed by Balarew and Duhlev [7] on the basis of Peason's hard and soft acids and bases (HSAB) concept [7,8]. They proposed that the sum of the χ-values $(\chi = H_{acid} \cdot H_{base})$ for all metals and ligands in the respective complexes $(\sum_i \chi_i = \sum_i (H_{acid} \cdot H_{base})_i)$ can be available not only as a criterion of stability of polyhedral complexes but also as an indication of determination of possible combination in the double salt crystals consisted of two kinds of discrete polyhedra, where H_{acid} and H_{base} denote the hardness value of acid and base, respectively [8].

Recent development of density functional theory (DFT) treated with Gaussian basis sets has made possible the accurate calculation of the energies and geometries of molecules even for weak interaction such as hydrogen bond at the same level as the post Hartree–Fock (HF) method [9]. Moreover, this method is computationally inexpensive in spite of its high accuracy due to exchange-correlation corrections. Recently, we also presented that in the double salt crystals containing two kinds of polyhedra, the comparison of sum of the formation energies (ΔE) of the respective coordination

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polyhedra that were geometrically optimized by the density functional calculations can be useful as non-empirical criterion in determining their coordination structures and combination [10,11].

The χ-value and the non-empirical analyses should be useful to examine a formation of $[CoCl_4(H_2O)]^{2-}$ in a double salt crystal system. However, it is regret that both analyses cannot be applied for the double salt $2RbCl \cdot CoCl_2 \cdot 2H_2O$, because it is not constructed of two kinds of isolated polyhedra. Among of several combinations for double salt crystals, the formation of $[CoCl_4(H_2O)_2]^{2-}$ and $[Mg(H_2O)_6]^{2+}$ complexes in $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$ has been predicted by Balarew [5] and Duhlev et al. [6]; they indicated that their conformations were estimated to be quite appropriate from the χ-value and non-empirical analyses. Thus, the crystal structure analysis of $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$ has been performed by using X-ray diffraction method, and the geometry optimizations for octahedral $[MCl_4(H_2O)_2]^{2-}$ and $[M(H_2O)_6]^{2+}$ ($M =$ Mg, Co) complexes have been carried out by the ab initio density functional methods in order to understand the complex formation in $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$ crystal, especially to explain the formation of unique $[CoCl_4(H_2O)_2]^{2-}$ complex in the double salt.

2. Methods

2.1. X-ray structure determination

Ternary system $CoCl_2$–$MgCl_2$–H_2O [12] has been prepared as dark purple plate-like crystals suitable for the X-ray diffraction study from the aqueous solution by slow evaporation of the solvent. Crystal data and experimental details for $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$ are listed in Table 1. Diffraction data were collected with an Enraf–Nonius CAD4 four-circle diffractometer using graphite monochromated Mo$K\alpha$ radiation. The intensities were monitored by three standard reflections every 2 h. There was no significant variation in intensities during the data collections. The intensities were converted to Fo data in the usual manner. All the reflections were corrected for Lorentz and polarization effects. Non systematic absences for reflections led to two possible space groups, $P1$ and $P\bar{1}$. The centrosymmetric space group $P\bar{1}$ was confirmed as the correct one by the successful refinement. The structure was solved by the heavy atom method and refined by the full matrix least-squares method. An empirical absorption correction using DIFABS [13] was applied after isotropic refinement. Several cycles of refinements including anisotropic thermal parameters for non-hydrogen atoms were carried out. All H atoms were located by the Fourier difference synthesis and were refined isotropically. Difference-Fourier maps calculated using

Table 1
Crystallographic data for $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$

Molecular weight	369.04
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	6.0976(9)
b (Å)	6.308(1)
c (Å)	8.579(3)
α (deg)	81.99(2)
β (deg)	88.40(2)
γ (deg)	84.61(1)
V (Å^3)	325.3(10)
Z	1
T (K)	253
$F(000)$	187
$D_{calc.}$ (g cm^{-3})	1.884
Radiation (Mo$K\alpha$) (Å)	0.71069
Crystal size (mm)	$0.3 \times 0.3 \times 0.4$
μ (Mo$K\alpha$) (cm^{-1})	22.0
Unit cell determination	25 reflections
Scan mode	$\omega - 2\theta$
Maximum 2θ	60
$h\,k\,l$ range	$\pm 8, \pm 8, +12$
Scanning rate (deg min^{-1})	4.0
Scan width (deg)	$1.10 + 0.35 \tan\theta$
Cutoff type	$|I_o| > 3\sigma|I_o|$
No. of independent reflections	2004
No. of reflections used	1873
Parameters refined	100
R	0.027
R_w	0.062
Weighting schemes	$1/\sigma^2(F_o)$

the final parameters showed maximum and minimum electron density peaks of 0.38 and $-0.97\,e\,\text{Å}^3$. Scattering factors and anomalous dispersion terms for non-hydrogen atoms were taken from the International Tables for X-ray Crystallography [14]. Calculations were performed on SGI O$_2$ workstation using the Enraf–Nonius Open MolEN program [15].

2.2. Density functional procedures

Ab initio calculations were performed according to the local spin density functional scheme by use of the DGauss program (the Dgauss program as part of the Unichem 3.0 software was used). The Gaussian-type orbital basis sets were used on the double-zeta-split-valence plus polarization (DZVP) level; (63321/531/41) for Co, (6321/411/1) for Cl, (6321/411/1) for Mg, (621/41/1) for O and (41) for H [16]. In calculations of electron density, exchange-correlation potential and exchange-correlation energy, the following types of three distinct auxiliary basis sets were also used for the respective atoms; (10/5/5) for Co, (9/4/4) for Cl, (9/4/3) for Mg, (7/3/3) for O and [4] for H [16]. The Vosko, Wilk and Nusair (VWN) potential [17] was used as a local spin density Hamiltonian. The accuracy of the analytical integral evaluation is 1×10^{-10} a.u., and the

corresponding accuracy of the numerical integration is 1×10^{-12} a.u. The SCF convergence thresholds are at 5×10^{-5} and 5×10^{-7} a.u. for the density and the total energy, respectively. The convergence criterion for the largest gradient component is at 8×10^{-4} a.u. The non-local corrections given by Becke [18] and Perdew [19] for exchange and correlation energies were applied after geometry optimizations at the level of local spin density calculations.

The initial distances between the central metal ion and coordinating atoms were set to be nearly equal to the sum of the corresponding radii of ions [20] and water molecules [21] in the starting octahedron of $[M(H_2O)_6]^{2+}$ and $[MCl_4(H_2O)]^{2-}$. Each central metal ion was located on the origin of the xyz-coordinates and the ligating atoms, L (L = O and Cl), were arranged along the x, y, and z axes. The O–H distance and H–O–H angle used for a water molecule are 0.95 Å and 105°, respectively. The initial orientation of the two hydrogen atoms of each water molecule in $[MCl_4(H_2O)_2]^{2-}$ was set in parallel to one of the rectangular axes, because the $[CoCl_4(H_2O)_2]^{2-}$ complexes found in the both double salts take such orientation.

We have recently reported the full geometry optimization for $[CoCl_4(H_2O)_2]^{2-}$ complex by the ab initio density functional calculations [22]. The most stable structure obtained, however, was distorted, which was explained in terms of formation of intramolecular hydrogen bonds of Cl···(H)O (see Fig. 4). So, in order to reproduce the octahedral structure of $[CoCl_4(H_2O)_2]^{2-}$ found here, the intramolecular hydrogen bonds must be blocked during the full geometry optimization process. Thus, in this work, the geometry optimizations for $[MCl_4(H_2O)_2]^{2-}$ complexes were carried out under the following constrained conditions: all angles of $L-M-L$ were fixed to be 90° or 180°, and the displacement of H atoms was restricted within the xy, yz, and xz planes. Optimizations for $[M(H_2O)_6]^{2+}$ complexes were also all carried out under the same conditions to ensure the same calculation accuracy as the $[MCl_4(H_2O)_2]^{2-}$ complexes optimized here, although the full optimizations of similar hydrate complexes calculated under alternative conditions have been reported in the previous paper [23,24].

Formation energy, ΔE, is defined as the difference between the total energy of the complexes, $E([M(H_2O)_6]^{2+})$ and $E([MCl_4(H_2O)_2]^{2-})$, and the sum of the energies of the respective constituents, $E(M^{2+})$, $E(H_2O)$, and $E(Cl^-)$, as follows:

$$\Delta E([M(H_2O)_6]^{2+}) = \{E(M^{2+}) + 6E(H_2O)\} - E([M(H_2O)_2]^{2+}),$$

$$\Delta E([MCl_4(H_2O)_2]^{2-}) = \{E(M^{2+}) + 2E(Cl^-) + 2E(H_2O)\} - E([MCl_4(H_2O)_2]^{2-}).$$

The energy of -76.4223 a.u. was used for a water molecule optimized as an isolated molecule having the O–H bond length of 0.98 Å and the H–O–H angle of 104°. All density functional calculations were performed with SGI Indy workstation.

3. Results and discussion

3.1. Structure of $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$

The final atomic parameters are summarized in Table 2. Selected interatomic distances and angles are listed in Table 3. The crystal structure successfully established by X-ray analysis contains well-separated $[CoCl_4(H_2O)_2]^{2-}$ and $[Mg(H_2O)_6]^{2+}$ octahedra in a unit cell (Fig. 1). ORTEP drawings [25] of the respective complexes are shown in Fig. 2 together with the atomic numbering and the selected interatomic distances.

The structure of $[CoCl_4(H_2O)_2]^{2-}$ had an octahedral geometry with four chloride atoms in the equatorial plane and two water molecules in the axial positions, which is quite unique in contrast to the tetrahedral $[CoCl_4]^{2-}$ that is generally recognized as a stable structure. The average Co–Cl distance (2.4768 Å) in $[CoCl_4(H_2O)_2]^{2-}$ is comparable to that obtained in $2RbCl \cdot CoCl_2 \cdot 2H_2O$ crystal (2.479 Å) [1]. On the other hand, it is slightly longer than those of *trans*- and *cis*-$[CoCl_2(H_2O)_4]$ complexes (2.445 and 2.414 Å, respectively) found in hydrate crystals of $CoCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 4H_2O$, respectively [26]. The elongation should be explainable by the decrease of charge on the cobalt cation coordinated with four Cl^- anions and an electrostatic repulsion among Cl^- ions within the equatorial plane. The Cl^- ions in $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$ connect to hydrogen atoms of water molecules of neighboring octahedral units as described in the latter section, although the ions in $2RbCl \cdot CoCl_2 \cdot 2H_2O$ were used for the formation of a distorted cubic polyhedron around the Rb^+ cation. The above finding indicates that Co–Cl distances are not so sensitive to an environment around $[CoCl_4(H_2O)_2]^{2-}$ complex. On the other hand, the Co–O distance for $[CoCl_4(H_2O)_2]^{2-}$ (2.043 Å) in $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$ double salt crystal is shorter than not only those for *trans*-$[CoCl_2(H_2O)_4]$ (2.081 Å) in $CoCl_2 \cdot 6H_2O$ and *cis*-$[CoCl_2(H_2O)_4]$ (2.110 Å (av.)) in $CoCl_2 \cdot 4H_2O$ [26] but also that for $[CoCl_4(H_2O)_2]^{2-}$ (2.110 Å) in $2RbCl \cdot CoCl_2 \cdot 2H_2O$ [1]. The difference in the Co–O bond lengths for the $[CoCl_4(H_2O)_2]^{2-}$ complexes between $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$ and $2RbCl \cdot CoCl_2 \cdot 2H_2O$ crystals indicates that the Co–O distance is more sensitive to the environment around the octahedron than the Co–Cl bond. The average Mg–O distance (2.064 Å) in the octahedral $[Mg(H_2O)_6]^{2+}$ is comparable to those found in other double salt crystals such as $MnCl_2 \cdot 2MgCl_2 \cdot 12H_2O$ (2.071 Å) [10], $CaCl_2 \cdot$

Table 2
Atomic coordinates and thermal parameters for $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$[a]

Atom ($\mathring{A}^2$)	x	y	z	B_{eq} or B_{ios}
Co	0	0	0	1.629(4)
Cl(1)	−0.11173(7)	−0.03795(7)	0.28162(4)	2.876(7)
Cl(2)	0.25540(6)	0.26541(6)	0.04935(5)	2.511(6)
Mg	0.5	0.5	0.5	1.95(1)
O(1)	0.2473(2)	−0.2390(2)	0.0535(2)	2.48(2)
O(2)	0.4041(2)	0.8049(2)	0.3892(2)	3.23(2)
O(3)	0.6940(3)	0.4399(2)	0.3081(1)	3.24(2)
O(4)	0.2359(2)	0.3752(2)	0.4094(2)	3.43(2)
H(1A)	0.230(9)	−0.363(6)	0.045(5)	10(1)
H(1B)	0.364(5)	−0.214(5)	0.042(4)	5.5(7)
H(2A)	0.496(5)	0.879(5)	0.349(3)	4.9(6)
H(2B)	0.280(6)	0.806(5)	0.375(4)	6.7(8)
H(3A)	0.741(8)	0.558(8)	0.238(5)	10(1)
H(3B)	0.723(5)	0.306(5)	0.300(4)	4.8(6)
H(4A)	0.226(5)	0.318(4)	0.328(3)	3.9(5)
H(4B)	0.150(5)	0.291(4)	0.472(3)	4.2(6)

[a] $B_{eq} = (4/3)(a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab\cos c\beta(1,2) + ac\cos b\beta(1,3) + bc\cos a\beta(2,3)$. H atoms were refined isotropically.

Table 3
Selected interatomic distances ($\mathring{A}$) and angles (deg)

$[CoCl_4(H_2O)_2]^{2-}$			
Co–Cl(1)	2.4773(4)	Co–Cl(1)[a]	2.4773(4)
Co–Cl(2)	2.4762(4)	Co–Cl(2)[a]	2.4762(4)
Co–O(1)	2.043(1)	Co–O(1)[a]	2.043(1)
Cl(1)–Co–Cl(1)[a]	180	Cl(1)–Co–Cl(2)	89.39(1)
Cl(1)–Co–Cl(2)[a]	90.61(1)	Cl(1)–Co–O(1)	89.15(4)
Cl(1)–Co–O(1)[a]	90.85(4)	Cl(1)[a]–Co–Cl(2)	90.61(1)
Cl(1)[a]–Co–Cl(2)[a]	89.39(1)	Cl(1)[a]–Co–O(1)	90.85(4)
Cl(1)[a]–Co–O(1)[a]	89.15(4)	Cl(2)–Co–Cl(2)[a]	180
Cl(2)–Co–O(1)	88.97(3)	Cl(2)–Co–O(1)[a]	91.03(3)
Cl(2)[a]–Co–O(1)	91.03(3)	Cl(2)[a]–Co–O(1)[a]	88.97(3)
O(1)–Co–O(1)[a]	180		
$[Mg(H_2O)_6]^{2+}$			
Mg–O(2)	2.063(1)	Mg–O(2)[b]	2.063(1)
Mg–O(3)	2.058(1)	Mg–O(3)[b]	2.058(1)
Mg–O(4)	2.073(2)	Mg–O(4)[b]	2.073(2)
O(2)–Mg–O(2)[b]	180	O(2)–Mg–O(3)	90.24(5)
O(2)–Mg–O(3)[b]	89.76(5)	O(2)–Mg–O(4)	91.75(6)
O(2)–Mg–O(4)[b]	88.25(6)	O(2)[b]–Mg–O(3)	89.76(5)
O(2)[b]–Mg–O(3)[b]	90.24(5)	O(2)[b]–Mg–O(4)	88.25(6)
O(2)[b]–Mg–O(4)[b]	91.75(6)	O(3)–Mg–O(3)[b]	180
O(3)–Mg–O(4)	91.18(6)	O(3)–Mg–O(4)[b]	88.82(6)
O(3)[b]–Mg–O(4)	88.82(6)	O(3)[b]–Mg–O(4)[b]	91.18(6)
O(4)–Mg–O(4)[b]	180		

Equivalent positions: [a] $-x, -y, -z$; [b] $-x+1, -y+1, -z+1$.

$2MgCl_2 \cdot 12H_2O$ (2.059 $\mathring{A}$) [27], and $MgCl_2 \cdot 6H_2O$ (2.060 $\mathring{A}$) [28]. These facts indicate that the structure of complex $[Mg(H_2O)_6]^{2+}$ is structurally rigid to environments of outer sphere.

All the octahedra in the double salt crystal are linked to each other by hydrogen bonds. The hydrogen bond distances and angles are given in Table 4. All hydrogen atoms participate in formation of hydrogen bond networks. The $Cl \cdots (H)O$ type hydrogen bonds in this crystal are within the range of 3.127(1)–3.380(1) $\mathring{A}$, as shown in Table 4. The average $Cl \cdots (H)O$ hydrogen bond distance (3.242 $\mathring{A}$) is comparable to those reported previously; for example, 3.187 $\mathring{A}$ in $2RbCl \cdot CoCl_2 \cdot 2H_2O$ [1], 3.196 $\mathring{A}$ in $MnCl_2 \cdot 2MgCl_2 \cdot 12H_2O$ [10],

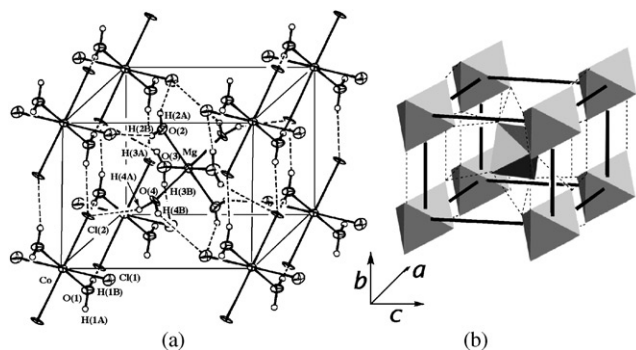Fig. 1. Crystal structure of $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$ in a unit cell. (a) An ORTEP drawing: non-H and H atoms are represented by thermal ellipsoids scaled at 30% probability level and small circles with 0.1 Å radius, respectively. (b) Coordination polyhedron diagram: light and dark shaded octahedra are $[CoCl_4(H_2O)_2]^{2-}$ and $[Mg(H_2O)_6]^{2+}$, respectively. Dotted lines in both drawings denote hydrogen bonds.
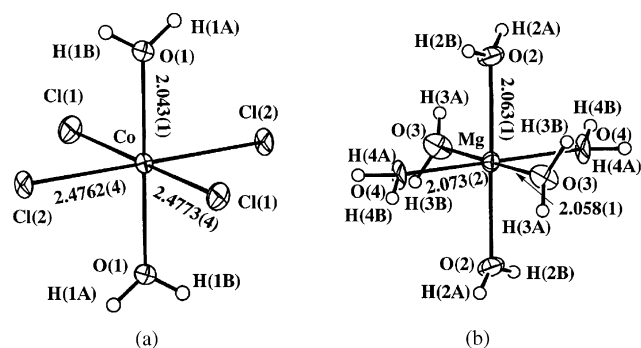

Fig. 2. ORTEP drawings [25] of the structures for $[CoCl_4(H_2O)_2]^{2-}$ (a) and $[Mg(H_2O)_6]^{2+}$ (b) complexes in the double salt $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$, which are drawn with thermal ellipsoids scaled at 30% probability level. H atoms are drawn by small circles with 0.1 Å radius.

3.176 Å in $CoCl_2 \cdot 6H_2O$ [26], 3.200 Å in $CoCl_2 \cdot 4H_2O$ [26], 3.228 Å in $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$ [27], and 3.288 Å in $MgCl_2 \cdot 6H_2O$ [28].

3.2. Structures and formation energies of $[MCl_4(H_2O)_2]^{2-}$ and $[M(H_2O)_6]^{2+}$ optimized

3.2.1. Optimized structures

The structures of $[MCl_4(H_2O)_2]^{2-}$ and $[M(H_2O)_6]^{2+}$ optimized under the constrained condition are shown in Fig. 3. The M–Cl or M–O bond distances within the same molecule were equal to within ±0.1 Å, except for the Co–O bonds in the case of $[Co(H_2O)_6]^{2+}$ complex. The average Co–Cl distance (2.47 Å) for the $[CoCl_4(H_2O)_2]^{2-}$ polyhedra, as shown in Fig. 3(a), is comparable to those (2.477 and 2.437 Å) for $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$ and $2RbCl \cdot CoCl_2 \cdot 2H_2O$ [1], respectively, although the optimized Co–O distance (1.94 Å) is slightly shorter than those (2.043 and 2.107 Å) for $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$ and $2RbCl \cdot CoCl_2 \cdot 2H_2O$ [1], respectively.

Table 4
Hydrogen bond distances (Å) and angles (deg)

Hydrogen bond Cl · · · H–O	Distance Cl–O	Angle
Cl(2)[a] · · · H(1A)–O(1)	3.127	167
Cl(2)[b] · · · H(1B)–O(1)	3.130	156
Cl(1)[c] · · · H(2A)–O(2)	3.270	154
Cl(1)[d] · · · H(2B)–O(2)	3.324	158
Cl(2)[e] · · · H(3A)–O(3)	3.380	144
Cl(1)[f] · · · H(3B)–O(3)	3.170	166
Cl(2) · · · H(4A)–O(4)	3.255	160
Cl(1)[g] · · · H(4B)–O(4)	3.278	148

Equivalent positions: [a] $x, y-1, z$; [b] $-x+1, -y, -z$; [c] $x+1, y+1, z$; [d] $x, y+1, z$; [e] $-x+1, -y+1, -z$; [f] $x+1, y, z$; [g] $-x, -y, -z+1$.

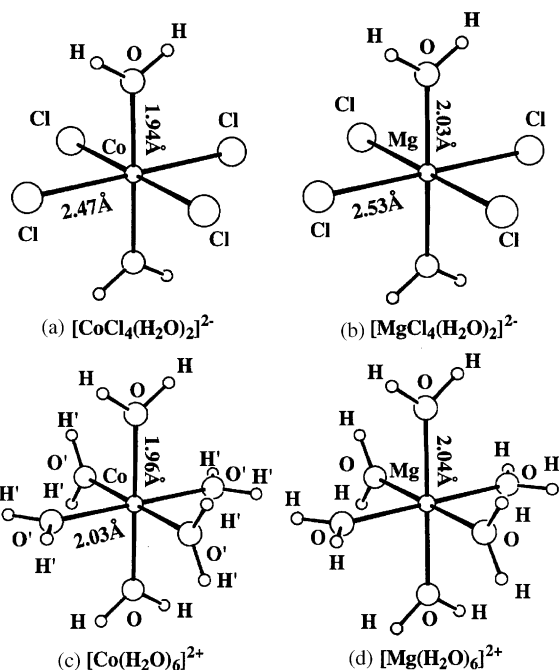Fig. 3. Structures of $[CoCl_4(H_2O)_2]^{2-}$ (a), $[MgCl_4(H_2O)_2]^{2-}$ (b), $[Co(H_2O)_6]^{2+}$ (c) and $[Mg(H_2O)_6]^{2+}$ (d) optimized under the constrained conditions.

Isolated $[MgCl_4(H_2O)_2]^{2-}$ complex has never been obtained experimentally. However, the average Mg–Cl distance (2.53 Å) in the optimized $[MgCl_4(H_2O)]^{2-}$ complex corresponds to those (2.517 and 2.506 Å) for $MgCl_6^{4-}$ with an octahedral arrangement in α-$MgCl_2$ [29] and β-$MgCl_2$ [30] crystals, respectively. The Mg–O bond distance (2.03 Å) in the $[MgCl_4(H_2O)]^{2-}$ complex seems to be slightly shorter than the values for $[Mg(H_2O)_6]^{2+}$ complexes found in the crystals such as $MgCl_2 \cdot 6H_2O$ (av. 2.060 Å [28]), $MnCl_2 \cdot MgCl_2 \cdot 12H_2O$ (av. 2.07 Å [10]), $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$ (av. 2.059 Å [27]) and $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$ (av. 2.065 Å (this work)).

In the structure of the $[Co(H_2O)_6]^{2+}$ complex optimized, three different Co–O bonds (2.03, 2.02 and 1.96 Å) were obtained. The difference among the Co–O distances is explainable in terms of the Jahn–Teller

distortion for Co^{2+} cation with d^7 electronic configuration at high spin state. The displacement (1.94–2.03 Å) for the Co–O distances obtained in the optimized complexes is slightly smaller than that (2.08–2.12 Å) for $[CoCl_2(H_2O)_4]$ complexes in $CoCl_2 \cdot 4H_2O$ and $CoCl_2 \cdot 6H_2O$ crystals [26] and that (2.06–2.12 Å) for $[Co(H_2O)_6]^{2+}$ in other crystals reported previously [31–34].

In the optimized $[Mg(H_2O)_6]^{2+}$, the Mg–O bond length (2.04 Å) also looks like slightly shorter than the values found in other crystals such as $MnCl_2 \cdot 2MgCl_2 \cdot 12H_2O$ (2.071 Å) [10], $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$ (2.059 Å) [27], and $MgCl_2 \cdot 6H_2O$ (2.060 Å) [28].

All the M–O distances calculated here (calculated in a vacuum system) are shorter than experimental values, although that of M–Cl reproduced well the experimental values, indicating that the M–O distances in the octahedral complexes should be sensitive to environments of the outer sphere.

As compared with the metal–ligand bond distances between the two optimized diaquatetrachloro complexes, $[CoCl_4(H_2O)_2]^{2-}$ and $[MgCl_4(H_2O)_2]^{2-}$, the bond lengths of Co–Cl (2.47 Å) and Co–O (1.94 Å) are significantly shorter than those of Mg–Cl (2.53 Å) and Mg–O (2.03 Å), respectively, although the ionic radius (0.745 Å) [20] of Co^{2+} in six-fold coordination is slightly larger than that (0.72 Å) of Mg^{2+}. However, this is understandable from the HSAB consideration, that is, the softer Co^{2+} cation expresses the stronger covalent property than the harder Mg^{2+} ion.

3.2.2. Formation energies of optimized $[MCl_4(H_2O)_2]^{2-}$ and $[M(H_2O)_6]^2$

The formation energies calculated for $[CoCl_4(H_2O)_2]^{2-}$ and $[MgCl_4(H_2O)_2]^{2-}$ complexes are 2451 and 2349 kJ mol^{-1}, respectively, as shown in Table 5, which are more stable than those of the corresponding hexaaqua complexes, 1363 kJ mol^{-1} for $[Co(H_2O)_6]^{2+}$ and 1334 kJ mol^{-1} for $[Mg(H_2O)_6]^{2+}$, respectively. Comparison of sum of the formation energies for the two possible combinations are also summarized in Table 5, together with the sum of the χ-values [7]. The χ-value of the former combination is larger than that of the

latter, indicating that the former is more stable than the latter. Although the physical meaning of the difference between their values, 29.44 and 22.83, is ambiguous, this is also supported from the comparison of the sum of the formation energies obtained by the ab initio calculations; the combination of $[Mg(H_2O)_6]^{2+}$ and $[CoCl_4(H_2O)_2]^{2-}$ complexes is more stable than that of $[MgCl_4(H_2O)_2]^{2-}$ and $[Co(H_2O)_6]^{2+}$ by 73 kJ mol^{-1}. In our calculations, any effects from the outer sphere of the complexes, such as hydrogen bonds and crystal packing, were not included. However, the former combination has been predicted to be stable on the basis of comparison of the non-empirically calculated formation energies, which has in fact been found in the double salt crystals. The above findings indicate that the energetic properties of the first coordination sphere play a decisive role in determining the constituent polyhedra in the double salt crystals.

3.3. A role of hydrogen bonds

The formation energy (2451 kJ mol^{-1}) for the $[CoCl_4(H_2O)_2]^{2-}$ complex optimized under the constrained conditions is less than that (2828 kJ mol^{-1}) for the distorted octahedral $[CoCl_4(H_2O)_2]^{2-}$ complex fully optimized (Fig. 4, Data from [22]) by 377 kJ mol^{-1}. This
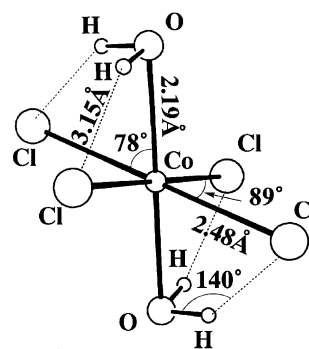

Fig. 4. Geometry of $[CoCl_4(H_2O)_2]^{2-}$ fully optimized (data from Ref. [22]). The O–Co–O angles to the equatorial plane defined by four Cl$^-$ ions are 78°. The optimized distances are 2.48 Å (av.) for Co–Cl and 2.19 Å (av.) for Co–O, respectively. Dotted lines indicate intramolecular hydrogen bonds, in which the Cl···O interatomic distances and Cl···H–O angles are 3.15 Å and 140°, respectively.

Table 5
Comparison of sum of the formation energies of the polyhedra

Combination of polyhedra	Sum of the formation energies (kJ mol^{-1})	Sum of the χ-values[a]
$[CoCl_4(H_2O)_2]^{2-}$–$[Mg(H_2O)_6]^{2+}$	3785	29.44
$[Co(H_2O)_6]^{2+}$–$[MgCl_4(H_2O)_2]^{2-}$	3712	22.83

[a] The sum of the χ-values for the respective complexes is defined as $\sum_i \chi_i = \sum_i (H_{acid} \cdot H_{base})_i$, which are calculated using the hardness parameters of acid (H_{acid}) and base (H_{base}). The values of H_{acid} and H_{base} are 2.53 for Mg^{2+} and 0.44 for Co^{2+}, and 0.94 for Cl$^-$ and 1.73 for H_2O, respectively [7].

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distortion is resulted from the intramolecular hydrogen bonds. Therefore, the most stable form of $[CoCl_4(H_2O)_2]^{2-}$ should be such a distorted octahedron. On the other hand, in the crystal structure of $CoCl_2 \cdot MgCl_2 \cdot 8H_2O$, there are eight kinds of $Cl^- \cdots H_2O$ hydrogen bonds, as listed in Table 4, and $[CoCl_4(H_2O)_2]^{2-}$ complex is connected to the neighboring complexes by 12 hydrogen bonds. Experimental formation energies of a single $Cl^- \cdots H_2O$ hydrogen bond is reported to be $62 \, kJ \, mol^{-1}$ [35], and thus the total energy of the twenty hydrogen bonds around $[CoCl_4(H_2O)_2]^{2-}$ could be roughly estimated to be $1200 \, kJ \, mol^{-1}$, which is enough to prevent the formation of regular octahedron of $[CoCl_4(H_2O)_2]^{2-}$ and to attain to the distorted form. The suitable hydrogen bonding networks around $[CoCl_4(H_2O)_2]^{2-}$ play an essential role in keeping the regular octahedral geometry.

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