Isolated versus Condensed Anion Structure VII: X-ray Structure Analysis of 1,3-Propanediammonium Dibromodichlorocadmate(II), $[H_3N(CH_2)_3NH_3]CdBr_2Cl_2$, and Estimation of Stability of Five-coordinated Halide Anions, MX_5^{3-} (M = Cd, Zn; X = Cl, Br) by Means of *Ab-initio* MO Calculations

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The coordination capability of Cl and Br in halogenocadmate(II) complexes is estimated by a solution of the structure of 1,3-propanediammonium dibromodichlorocadmate(II). The compound crystallizes as a layered anion structure with Cl bridges and Br terminals at 293 K: Imma, a = 741.56(7), b = 1869.5(5), and c = 771.55(8) pm, Z = 4. In order to explain the stronger tendency of halogenocadmate(II) complexes to form layered structures as compared to halogenozincate(II), *ab-initio* calculations were performed. The stability of MX_5^{3-} (M = Cd, Zn; X = Cl, Br) is compared. Isolated ZnX_5^{3-} and $CdBr_5^{3-}$ ions are not stable. On the other hand a trigonal bipyramid $CdCl_5^{3-}$ ion is considered to be subtly stable in the crystal mainly due to Coulomb attractive interactions between the positively charged metal cation Cd^{2+} in a $CdCl_3^-$ fragment and two Cl^- ions.

Key words: Crystal Structure; Halogenocadmate(II); *Ab-initio* MO Calculations.

Introduction

In recent studies of complex salts with bromocadmate(II) anions by X-ray diffraction and Br NQR, we found a variety of polymer anionic structure types [1 - 8] and an isolated $CdBr_4^{2-}$ tetrahedron [9, 10]. On the other hand, ZnX_4^{2-} (X = Cl, Br) complexes show a pronounced tendency to form only isolated tetrahedral anions [11]. For example $[M(NH_3)_6]ZnCl_5$ (M(III) = Co, Cr) has a structure that consists of a tetrahedral $ZnCl_4^{2-}$ ion with an additional Cl^- ion [12, 13]. $[M(NH_3)_6]CdCl_5$ (M(III) = Co, Cr) has, however, a trigonal bipyramid $CdCl_5^{3-}$ structure [14, 15]. We try to explain this discrepancy of Cd and Zn halide complexes by MO calculations. In addition, it seems that the bridging power of the halogen atoms in the Cd halide complexes is in the order Cl, Br > I [10], because layered compounds $[H_3N(CH_2)_3NH_3]CdX_4$ (X = Cl, Br) were found to be stable [16, 8] and $[H_3N(CH_2)_3NH_3]CdI_4 \cdot 2\,H_2O$ [10] has tetrahedral CdI_4^{2-} anions. We try to compare the bridging power of Cl and Br by forming a mixed halide complex with $[H_3N(CH_2)_3NH_3]^{2+}$ cation similar to the estimation of the bridging power of halogen atoms in Sb halide complexes [17].

Experimental

$[H_3N(CH_2)_3NH_3]CdBr_2Cl_2$, 1,3-propanediammonium dibromodichlorocadmate(II) was formed by mixing $[H_3N(CH_2)_3NH_3]CdBr_4$ with $[H_3N(CH_2)_3NH_3]CdCl_4$ with equal molar ratio in aqueous solution. Transparent planar crystals appeared from the solution. Chemical analysis (observed / calculated weight %): C(8.20/8.59), H(2.75/2.88), N(6.68/6.29).

The crystal structure was determined using a four-circle X-ray diffractometer, Enraf Nonius CAD4. From the measured intensities, corrected for Lorentz-polarization and absorption effects, the structure was solved by direct methods and Fourier syntheses, and

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Table 1. Experimental conditions for the crystal structure determination and crystallographic data of 1,3-propanediammonium dibromodichlorocadmate(II), $[H_3N(CH_2)_3NH_3]CdBr_2Cl_2$ (**1**), diffractometer Nonius CAD4; wavelength 71.093 pm (MoKα), monochromator: graphite (002); scan $\omega/2\theta$. (**1**): $C_3H_{12}Br_2CdCl_2N_2$ M = 419.26.

Crystal size/(mm^3)	0.4×0.3×0.075
Temperature/K	293(2)
Absorption coeff./(mm^{-1})	9.96
θ-range for data collected	$2.18 \leq \theta/° \leq 29.97$
Index ranges	$-10 \leq h \leq 0, -26 \leq k \leq 14,$ $0 \leq l \leq 10$
Space group	Imma (#74)
a/pm	741.56(7)
b/pm	1869.5(5)
c/pm	771.55(8)
$V \times 10^{-6}$/(pm^3)	1069.6(3)
Formula units Z	4
ρ_{cal}/(Mg m^{-3})	2.604
$F(000)$	784
Reflections collected	1423
Independent reflections	859 [R(int) = 0.0346]
Data ($I > 2\sigma(I)$)	751
Restraints/parameters	0/33
Goodness of fit on F^2	1.157
Final $R(I > 2\sigma(I))$	$R_1 = 0.0514$, $wR_2 = 0.1728$
R (all data)	$R_1 = 0.0583$, $wR_2 = 0.1802$
Largest diff. (peak, hole)/ (10^{-6}e(pm^3))	2.753 and −1.885
Max. and min. trans.	0.2600 and 0.0571
Extinction coeff.	0.0020(6)
Point positions	Cd in 4a, Br, N, C(1) in 8h, Cl in 8g, and C(2) in 4e,

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters U_{eq} for (1). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The temperature factor has the form: $T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*\}$. Anisotropic displacement parameters U_{ij} and atomic coordinates for hydrogen atoms are given elsewhere [24].

Atom	x	y	z	U_{eq}/(10^{-1}pm^2)
Cd	0	0	0	28(1)
Br	0	1403(1)	−500(2)	53(1)
Cl	2500	168(1)	2500	34(1)
N	5000	1170(5)	−191(14)	53(3)
C(1)	5000	1859(7)	739(19)	61(4)
C(2)	5000	2500	−270(21)	52(5)

refined by least-squares analysis with the programs given in [18].

Ab-initio molecular orbital calculation was performed using GAUSSIAN 98 programs [19]. Geometries of all stationary points including transition structures (TSs) were optimized at the Hartree-Fock level using the LANL2DZ basis set and using density functional theory (DFT) with Becke3LYP / LANL2DZ level [20]. The LANL2DZ basis set is a Los Alamos effective core potential (ECP) basis set of double-z quality (Hay and Wadt basis set) in the valence shell plus polarization function (DZVP) [21, 22]. Optimizations were performed utilizing gradient method without any geometrical constraint. All reactants and TS were tested by frequency analysis [23]. For stationary points, an energy minimum (reactant) and maximum point (TS) were characterized by the correct number of negative eigenvalue of their Hessian matrix, that is, the former and the latter have no and a single imaginary frequency, respectively.

Table 3. Bond distances (in pm) and bond angles (°) and hydrogen bond scheme. The hydrogen atoms have been determined in the least-squares refinements of the structures by fixing the bond lengths of X-H and bond angles in which atoms are involved.

Connection	d/pm	Connection	Angle/°
Cd-Br ×2	265.1(1)	Br-Cd-Br$^{\#1}$	180.0
Cd-Cl ×4	269.4(0)	Br-Cd-Cl	89.38(5)
		Br-Cd-Cl$^{\#1}$	90.62(5)
		Cl-Cd-Cl$^{\#1}$	180.0
		Cl-Cd-Cl$^{\#2}$	93.02(1)
		Cl-Cd-Cl$^{\#3}$	86.98(1)
		Cd-Cl-Cd$^{\#4}$	166.64(9)
C(1)-C(2) ×2	143(2)	C(2)-C(1)-N(1)	118(1)
C(1)-N(1) ×2	147(2)	C(1)-C(2)-C(1)$^{\#5}$	114(2)
		N(1)-C(1)-C(2)-C(1)$^{\#5}$	180.0

Hydrogen bond scheme

N-H···X	d(H···X)/pm	d(N···X)/pm	∠(N-H···X)/°
N-H(N1)···Cl ×2	266.6(7)	335.6(9)	135.1(2)
N-H(N2)···Br$^{\#6}$	294.7(11)	335.3(11)	109.7(8)
N-H(N3)···Br$^{\#7}$	294.7(11)	335.3(11)	109.7(8)

Symmetry code: $^{\#1}$ $-x, -y, -z$; $^{\#2}$ $x, -y, -z$; $^{\#3}$ $-x, y, z$; $^{\#4}$ $x + 1/2, -y + 1-1, z + 1/2$; $^{\#5}$ $x, -y + 1/2, z$; $^{\#6}$ $-x + 1/2, y, -z + 1/2 - 1$; $^{\#7}$ $-x + 1/2, y, -z - 1/2$.

Results and Discussion

1,3-Propanediammonium dibromodichlorocadmate(II) (**1**) is orthorhombic with space group D_{2h}^{28}-Imma at 293 K; the lattice constants etc. are listed in Table 1. Table 2 lists the positional coordinates and equivalent isotropic thermal parameters U_{eq} [24]. Intramolecular bond distances and angles are given in Table 3. In Fig. 1, the formula unit is drawn with

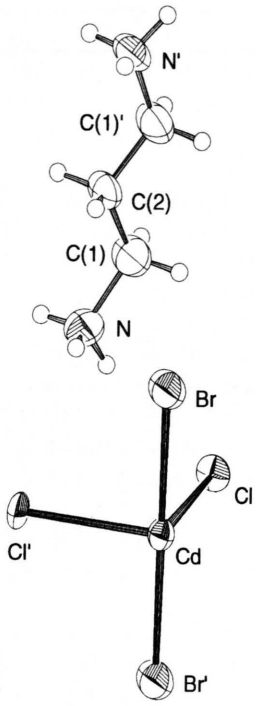

Fig. 1. The formula unit of 1,3-propanediammonium dibromodichlorocadmate(II) with the numbering of atoms. The anion is shown as part of bridged structures, the cation as a whole molecule. The thermal ellipsoids (50 % electrons as contour) are shown, too.

the numbering of atoms and the thermal ellipsoids. Figure 2 shows the projection of the unit cell along [100] onto the *bc* plane. The anion consists of a layered structure with Cl bridges and terminal Br atoms and anion layers are located on the *ac* plane at $b = 0$ and 1/2. Cd atoms have 4 bridging Cl at the distance of 269.4 pm and two Cd-Br bonds of 265.1 pm. Therefore, the Cd atom is surrounded by six halogen atoms with a distorted octahedral configuration: 2×Br and 4×Cl. Cations are located between anion layers and on the *bc* plane. The conformation of the cation is all staggered. They are connected to anions by hydrogen bonds, as shown in Fig. 2 and Table 3. This hydrogen network is similar to that of $[H_3N(CH_2)_3NH_3]CdBr_4$ and all of three hydrogen atoms of each ammonium group form hydrogen bonds with Cl or Br atoms and hydrogen bonds stabilize the layered structure of anions [8].

The stability of four ions ($ZnCl_5^{3-}$, $ZnBr_5^{3-}$, $CdCl_5^{3-}$, and $CdBr_5^{3-}$) was investigated here. LANL2DZ calculation shows that ZnX_5^{3-} ions (X = Cl, Br), having trigonal bipyramid (TBP) geometries,

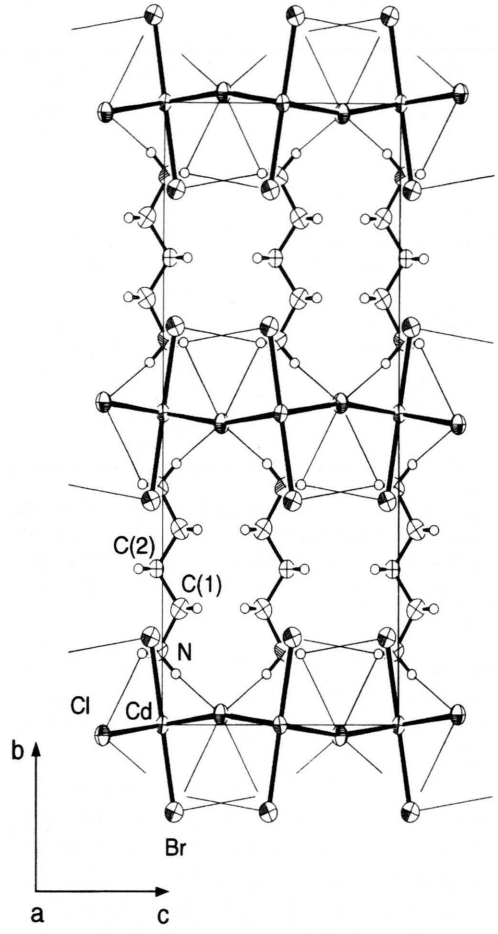

Fig. 2. The projection of the unit cell of (**1**) along [100] onto the *bc* plane. Hydrogen bonds are shown with thin lines.

are not stable and split into ZnX_4^{2-} (trigonal pyramid (TP)) and X^- ions or to planar MX_3^- and $2X^-$ fragments during geometry optimizations. Cadmium pentabromide ($CdBr_5^{3-}$) is also decomposed to give $CdBr_4^{2-}$ and Br^- ions. It is known that the ionic radii of Zn^{2+} and Cd^{2+} are 75 and 106 pm and those for halide ions Cl^- and Br^- are relatively larger, 181 and 195 pm, respectively. These data suggest that Zn^{2+} is too small for large halide ions to form TBP type five-coordinated geometry. Also for $CdBr_5^{3-}$ species, Cd^{2+} must be too small to be coordinated by five bromine atoms to attain TBP geometry. The single point energy evaluations in the range of 220 - 400 pm for breaking M-X (M = Zn, Cd and X = Cl, Br) bond revealed that the potential energy curves show monotonous downhill leading to the separated two (MX_4^{2-} and X^-) or three fragments (MX_3^- and

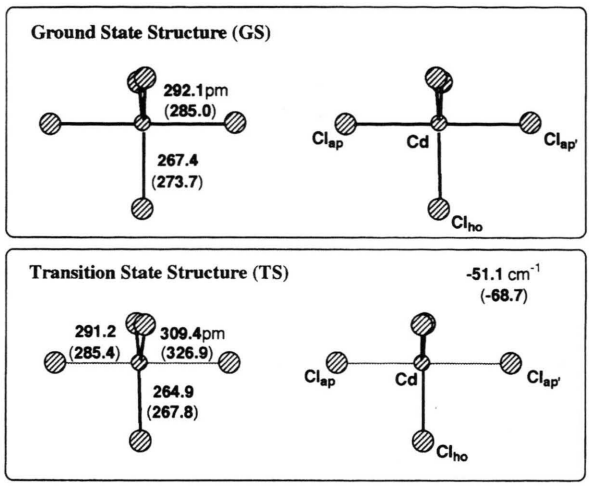

Fig. 3. The stetreoviews of LANL2DZ optimized ground state structure (GS) and transition state structure (TS) are shown. The structures are optimized without any geometrical constraint. The values in parentheses are at Becke3LYP/LANL2DZ.

$2X^-$) as mentioned above. In fact, the existence of the compounds including three MX_5^{3-} species ($ZnCl_5^{3-}$, $ZnBr_5^{3-}$, and $CdBr_5^{3-}$) has not been reported yet experimentally and the attempts to synthesize the compounds with these species were not successful in our laboratory until now. Only the compounds with a $CdCl_5^{3-}$ unit could be isolated and the structures were determined by X-ray analysis [14].

The ground state structure of $CdCl_5^{3-}$ could exist only at the sophisticated level (see upper section in Fig. 3 after the broad search with available calculation levels implemented in GAUSSIAN 98 [25]. Atomic distances of two apical Cd-Cl and three equatorial Cd-Cl bond lengths are 292.1 and 267.4 pm, respectively. These ground state form is decomposed into $CdCl_4^{2-}$ and Cl^- by passing through distorted trigonal bipyramidal TS, which is shown in the lower section in Fig. 3 (the bond lengths are 309.4 pm for breaking apical $Cd\cdots Cl_{ap'}$, 291.2 pm for the other apical Cd-Cl_{ap}, and 264.9 pm for three equatorial Cd-Cl_{eq} bonds and bond angles are 180.0° for Cl_{ap}-Cd-$Cl_{ap'}$, 90.8° for Cl_{ap}-Cd-Cl_{eq}, 89.2° for $Cl_{ap'}$-Cd-Cl_{eq}, and 120.0° for Cl_{eq}-Cd-Cl_{eq}). The activation energy ($\Delta E^{\#}$) is evaluated to be extremely small (< 1 kJ/mol at LANL2DZ//LANL2DZ and 1.94 kJ/mol at Becke3LYP/LANL2DZ//Becke3LYP/LANL2DZ) as the energy difference between this TS and the ground state. The number of single imaginary frequency is calculated to be only –51.1 (–68.7) cm^{-1}, respectively. This vibrational mode clearly shows the bond breaking between Cd and $Cl_{ap'}$ atoms. Judging from these computational results (that is, extremely low activation energy, small number of single imaginary frequency, or the shallow potential curve through the TS leading to $CdCl_4^{2-}$ and Cl^-), the formation of a trigonal bipyramidal molecule of $CdCl_5^{3-}$, which is experimentally observed in crystals, is considered to be attributable to Coulomb attractive interaction between a positively charged metal cation Cd^{2+} in a $CdCl_3^-$ fragment and two Cl^- ions. Two Cl^- ions are located on the opposite side of a planar $CdCl_3^-$ fragment. The positioning of the atoms in crystals must be definitely affected by the crystal packing. This computational result that TBP type $CdCl_5^{3-}$ species is unstable in the gas phase suggests that pentachlorocadmate (II) can exist only as an assembly of a $CdCl_3^-$ unit and two Cl^- ions in crystals rather than just a single fragment of $CdCl_5^{3-}$, as though it looks like TBP shape.

The geometry optimizations (LANL2DZ) of MX_4^{2-} species ($CdCl_4^{2-}$, $CdCl_2Br_2^{2-}$, and $CdBr_4^{2-}$) suggest that tetrahedral geometry is quite stable for each ion. The LANL2DZ (Becke3LYP / LANL2DZ) activation energies calculated on the LANL2DZ (Becke3LYP / LANL2DZ) geometries for the decomposition of $CdCl_4^{2-}$ to $CdCl^{3-}$ and Cl^- ions, that for $CdCl_2Br_2^{2-}$ to $CdCl_2Br^-$ and Br^-, that for $CdCl_2Br_2^{2-}$ to $CdClBr_2^-$ and Cl^-, and that for $CdBr_4^{2-}$ to $CdBr_3^-$ and Br^- were evaluated to be +93.7 (+99.2), +65.3 (+65.7), +102.1 (+105.4), and +72.0 (+72.8) kJ/mol [26], respectively, indicating the M-X bonds are considerably strong and have fundamentally coordinating but significantly covalent nature. The LANL2DZ and Becke3LYP / LANL2DZ geometrical parameters and energies are quite similar for all three ions considered here.

The geometry optimization (both at the LANL2DZ and Becke3LYP/LANL2DZ levels) of six-coordinated octahedral $CdCl_4Br_2^{4-}$ (two Br atoms are positioned at apical) gave three fragments ($CdCl_4^{2-}$ and two Br^- ions) and the optimizations of CdX_6^{4-} (X=Cl and Br) also decomposed into several fragments, indicating that in the gas phase six-coordinated species are very unstable (the activation energies to decompose tetrahedral complexes were evaluated to be > 84 kJ/mol as mentioned above). The computational results (for example, almost no activation energies for the breaking of Cd-X bond in CdX_6^{4-} species) suggest that the geometries of the complex

salts observed in crystals are due to Coulomb interaction between cationic metal and anionic halogen atoms, and more importantly to crystal packing to gather constituent fragments and less to interactions between orbitals.

Thus, it is concluded that tetrahedral (T_d) ions CdX_4^{2-} are quite stable and the coordinate bonds for Cd-X are highly covalent. In fact, many experimental illustrations for structural analysis of compounds including tetrahedral CdX_4^{2-} species have been reported [9, 10]. On the other hand, trigonal bipyramidal (TBP) CdX_5^{3-} and octahedral (O_h) CdX_6^{4-} ions are relatively unstable and easily decompose into several fragments during geometry optimization. These results suggest that weak Coulomb interaction between metal cation Cd^{2+} and anionic ligands X^- in $CdX_n^{(n-2)-}$ ions and/or steric factor to achieve crystal packing appear to be important factors to maintain TBP or O_h shaped coordination.

As shown in Fig. 2, two Cl ligands in $CdCl_2Br_2^{2-}$ species connect a Cd atom with Cd in another molecule, making basically a two-dimensional planar structure. The stacking of these planar units make up a layered structure, forming the cavity to accept counter cations between layers in the crystal as shown in Figure 2. Counter cation (1,3-propanediammonium ion $[NH_3\text{-}(CH_2)_3\text{-}NH_3]^{2+}$) can be held in the cavity and larger Br atoms located at apical positions work as the wall to hold the counter cation in the cavity. The terminal Br and bridging Cl atoms make hydrogen bonds with $\text{-}NH_3^+$ protons. These hydrogen bonds work as anchors to stabilize cations in the cavity and to make the complexes (crystals) stable.

X-ray crystallographic analysis shows that there are few crystalline solids having layered structure of CdX_n units, suggesting that a combination of anion and cation species is very sensitive to achieve layered structures in crystals and the mismatch of them lead to a non-layered structure, in which four- or five-coordinated species of Cd are included [8 - 10, 27]. Since the size of counter cation held between the layers appears to be very important and very sensitive, the search for cations are now going on by using molecular modeling method.

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[24] Tables of the atomic coordinates including hydrogen atoms, thermal parameters, bond distances and angles have been deposited as CCDC 164997 for (**1**) at the Cambridge Crystallographic Data Center.

[25] The ground state geometries for all compounds $ZnCl_5^{3-}$, $ZnBr_5^{3-}$, $CdCl_5^{3-}$, and $CdBr_5^{3-}$ could be located at semi-empirical PM3 level. However, the computational levels are clearly poor to investigate the structures of coordination compounds. As reference data, the geometrical parameters ($M\text{-}X_{ap}$ and $M\text{-}X_{ho}$ lengths and $X_{ap}\text{-}M\text{-}X_{ap}$ angle) are shown: $ZnCl_5^{3-}$: 243.2 pm, 238.2 pm, 180.0°; $ZnBr_5^{3-}$: 255.3 pm, 250.0 pm, 180.0°; $CdCl_5^{3-}$: 257.2 pm, 254.1 pm, 180.0°; $CdBr_5^{3-}$: 279.1 pm, 277.9 pm, 180.0°.

[26] The breaking bond lengths (pm) and the number of single imaginary frequency (cm^{-1}) for the LANL2DZ (Becke3LYP/LANL2DZ) TSs for the decomposition of tetrahedral CdX_4^{2-} species into CdX_3^- and X^- are as follows: $CdCl_4^{2-}$ to $CdCl_3^-$ and Cl^-, 478.3(500.7) pm and –47.2 (–44.5) cm^{-1}; $CdCl_2Br_2^{2-}$ to $CdCl_2Br^-$ and Br^-, 480.6 (490.8) and –34.4 (–35.2); $CdCl_2Br_2^{2-}$ to $CdClBr_2^-$ and Cl^-, 484.7 (512.3) and –45.4 (–41.0); $CdBr_4^{2-}$, 485.9 (498.1) and –33.3 (–33.6).

[27] $[NH_2(CH_3)_2]_2CdBr_4$: A. Waskowska, Z. Kristallogr. **209**, 752(1994); $[N(CH_3)_4]_2CdBr_4$: T. Asahi, K. Hasebe, and K. Geshi, J. Phys. Soc. Japan **61**, 1590 (1992); Cs_2CdBr_4 and $[CH_3NH_3]_2CdBr_4$: S. Altermatt, H. Arend, A. Niggli, and W. Petter, Mat. Res. Bull, **14**, 1391 (1979).