Cluster Compounds

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Structure of a Discrete Dichloride Hexahydrate Cube as a Tris(diisopropylamino)cyclopropenium Salt**

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The aqueous solvation of halide anions, and the chloride anion in particular, is a highly active area of research, since these are among the most common anions in nature. The energetics and structures of chloride–water clusters are important to our understanding of solvation phenomena.[1] For example, solvated anions are relevant to the study of the interfaces of aqueous salt solutions with air, biologically important water–membrane interfaces, electrical phenomena in the troposphere and ionosphere, and the mobility of ions. Consequently, chloride hydrates have been investigated by a large number of experimental and theoretical techniques.[2] Almost all of these studies have focused on monochloride hydrates $[Cl(H_2O)_n]^-$, and they have addressed issues such as the stabilities and structures (including the coordination number and location of the chloride anion) of the complexes, as well as their infrared spectra. Owing to the tendency of chloride anions to be located on the cluster surfaces, these monochloride hydrate clusters invariably have low-energy polar structures.[2]

In contrast, the study of dichloride hydrates is almost unknown. To our knowledge, no theoretical studies and only one brief structural report of a discrete dichloride hydrate cluster have been published.[3] Dichloride clusters have a greater potential to form nonpolar clusters. They are relevant in concentrated solutions and may be even more relevant in hydrophobic and low-polarity environments. We now report on structural and theoretical studies of the nonpolar cluster $[Cl_2(H_2O)_6]^{2-}$ ($\mathbf{1}^{2-}$).

The solid-state structure of $[C_3(N\textit{i}Pr_2)_3]Cl\cdot 3H_2O$ was initially determined to investigate the effect of anticipated steric interactions between the isopropyl groups in the previously unknown tris(diisopropylamino)cyclopropenium cation (Figure 1). Other aminocyclopropenium cations contain nitrogen atoms in planar coordination environments; however, steric interactions in $[C_3(N\textit{i}Pr_2)_3]^+$ force two of the isopropyl groups out of the C_3N_3 plane, and one of the nitrogen atoms (N2) assumes a distorted tetrahedral coordination geometry. The structure of this and related cations will be discussed elsewhere.[4]

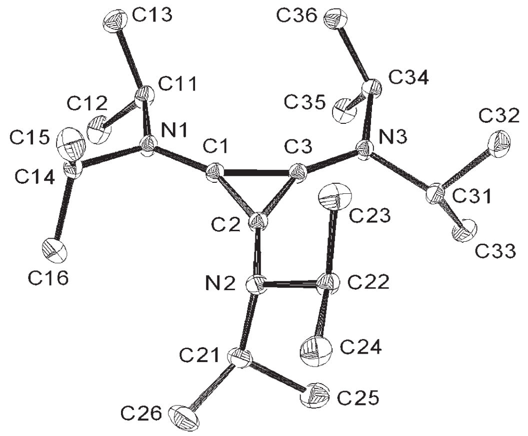

Figure 1. The cation in $[C_3(N\textit{i}Pr_2)_3]Cl\cdot 3H_2O$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected interatomic distances [Å] and angles [°]: C1–C2 1.3861(8), C1–C3 1.4316(9), C2–C3 1.3881(8), N1–C1 1.3219(7), N2–C2 1.3928(8), N3–C3 1.3260(8); C2-N2-C21 109.57(5), C2-N2-C22 113.83(5), C21-N2-C22 118.99(5).

To our surprise, the chloride anion in $[C_3(N\textit{i}Pr_2)_3]Cl\cdot 3H_2O$ was found as the discrete dichloride hexahydrate cluster $\mathbf{1}^{2-}$ (Figure 2), in which the chloride anions occupy opposite corners of the Cl_2O_6 cube. Effectively, each chloride anion has

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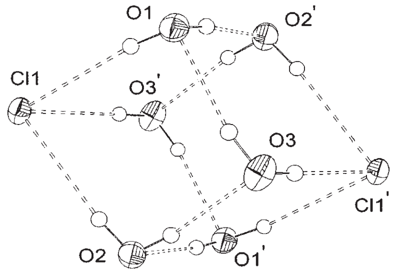

Figure 2. The cluster $\mathbf{1}^{2-}$ in $[C_3(N\mathit{i}Pr_2)_3]Cl\cdot 3\,H_2O$. One of the two possible hydrogen-bonding arrangements is shown; dashed lines indicate hydrogen bonds. Thermal ellipsoids are set at 50% probability. Selected interatomic distances [Å] and angles [°]: Cl1–O1 3.2529(8), Cl1–O2 3.2413(8), Cl1–O3′ 3.1860(8), O1–O3 2.8345(11), O2–O3 2.8245(11), O1–O2′ 2.8379(11), Cl1–Cl1′ 6.3212(5); O1-Cl1-O2 77.02(2), O1-Cl1-O3′ 74.07(2), O2-Cl1-O3′ 72.56(2), O1-O3-O2 91.21(3), O3-O1-O2′ 84.22(3), O3-O2-O1′ 86.46(3).

another chloride anion in its third solvation sphere. Every edge of the cube contains one hydrogen atom, and there are no hydrogen atoms exterior to the cluster. Thus, each chloride anion is involved in three hydrogen bonds. Each oxygen atom has one hydrogen bond to a chloride anion, one hydrogen bond to an oxygen atom, and one hydrogen bond from another oxygen atom. There are two possible hydrogen-bonding arrangements around the O_6 ring (one is shown in Figure 2), each with (noncrystallographic) S_6 symmetry. If the hydrogen-atom positions are averaged, the symmetry of the ring is D_{3d}. The O_6 cluster has a distorted chair conformation, with the axial hydrogen atoms hydrogen bound to the chloride anions. Note that the chloride anions are not encapsulated by water molecules, but can be considered as surface anions.

There has been one report of such a discrete cube:[3] Dalley and co-workers reported $\mathbf{1}^{2-}$ as a salt of sodium [2.2.2]cryptand (Crypt-222; Cambridge Structural Database (CSD) reference code ZOMBAE).[5] A dichloride hexahydrate cube with hydrogen bonding to a cationic complex has been characterized (CHYDNI),[6] and a dibromide hexahydrate cube has also been reported as part of a hydrogen-bonding network (KIQVAH).[7] The salt [K(Crypt-222)]Br·3.5 H_2O has disordered cubes of water molecules and bromide anions as part of a hydrogen-bonding network.[8] An interesting "inverted" $[Na_2(H_2O)_6]^{2+}$ cube within a network of hydrogen bonds has also been reported.[9]

Table 1 gives selected distances and angles for our $\mathbf{1}^{2-}$ anion and for other $[X_2(H_2O)_6]^{2-}$ (X = Cl, Br) cubes. The Cl–O distances for the three chloride cubes are similar, with the distances in CHYDNI being approximately 0.1 Å shorter than those in the other two. The O–O distances in three of the cubes are very similar (2.790–2.888 Å), but those in ZOMBAE (3.063 Å) are noticeably longer. The $[Na_2(H_2O)_6]^{2+}$ cube has an average O–O distance of 2.787 Å.[9] A crystallographically characterized $(H_2O)_8$ water cube also has a similar average O–O distance (2.85 Å), although considerable variation in the distances (2.750–2.929 Å) results from the interaction of the exterior hydrogen atoms with the cocrystallized cobalt complexes.[10] The most remarkable difference between the chloride cubes lies with the Cl–Cl distance, for which ours is the longest at 6.3212(5) Å, compared to 5.953 Å in ZOMBAE and 5.204 Å in CHYDNI. These differences largely result from the differing angles in the cubes: the O-Cl-O angles in our structure are approximately 10° smaller than those in the two other chloride cubes; the O-O-O angles in our structure are approximately 10° smaller than those in CHYDNI, but are more similar to those in ZOMBAE. The origin of the structural differences between the three $\mathbf{1}^{2-}$ clusters must be a combination of crystal-packing forces (differing electrostatic arrangements) and steric interactions, as well as the external hydrogen-bonding interactions in CHYDNI.

Table 1: Selected average structural parameters for $[X_2(H_2O)_6]^{2-}$ clusters.

	This work	ZOMBAE[5]	CHYDNI[6]	KIQVAH[7]
X	Cl⁻	Cl⁻	Cl⁻	Br⁻
X–X [Å]	6.321	5.953	5.204	7.057
X–O [Å]	3.227	3.206	3.120	3.428
O–O [Å]	2.832	3.063	2.790	2.888
O-X-O [°]	74.55	83.11	85.63	68.41
O-O-O [°]	87.30	87.96	98.96	83.57

As can be seen in Figure 3, $\mathbf{1}^{2-}$ is well-isolated from the cationic centers in $[C_3(N\mathit{i}Pr_2)_3]Cl\cdot 3\,H_2O$: the chloride anions are surrounded by isopropyl groups, and the closest interactions between the cluster and the C_3^+ ring involve O1 and

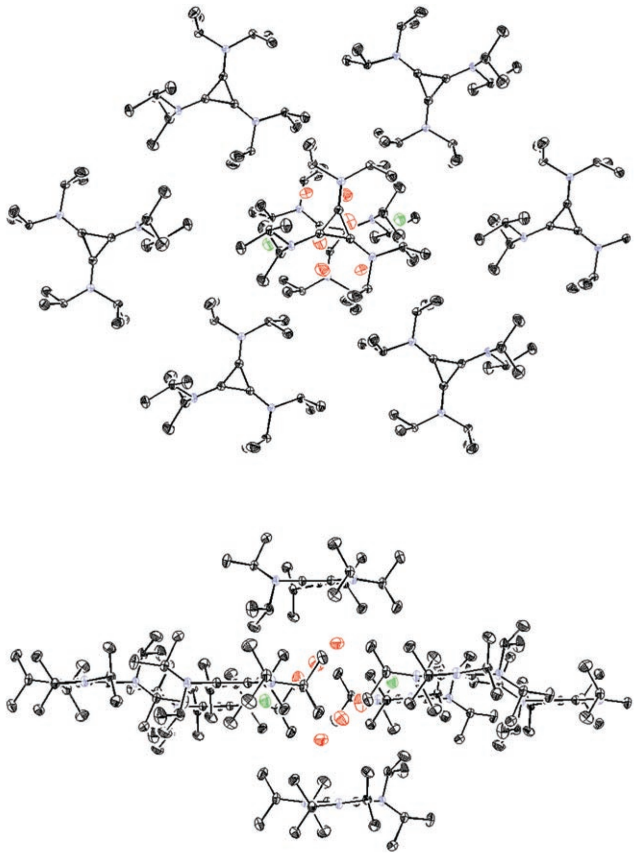

Figure 3. Two orthogonal views of $[C_3(N\mathit{i}Pr_2)_3]Cl\cdot 3\,H_2O$ illustrating the environment of $\mathbf{1}^{2-}$ (Cl green, O red, N blue, C black). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability.

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O1′ (above and below the ring; O1−C1 = 3.1488(9) Å, O1−C2 = 3.5190(9) Å, and O1−C3 = 3.2460(9) Å). Most of the contacts between the chloride anion and the cyclopropenium cation involve the methyl groups (C12, C24, C25, and C33 at C−Cl distances of 3.85–4.0 Å), with the exception of a contact to the hydrogen atom on C34, which is in the α position with respect to a nitrogen atom. For this contact, the Cl−H distance is 2.94 Å, and the C-H-Cl angle is 146.6°. Weiss and coworkers have commented on the electron-rich nature of tris(dialkylamino)cyclopropenium cations and the resultant ion-pair strain between the cations and halide anions, which leads to isolated anions.[11] We might, therefore, expect our cluster to be less distorted from the ideal gas-phase structure than the other known clusters, especially that in CHYDNI, which is involved in external hydrogen bonding.

To investigate the low-energy gas-phase structure of $\mathbf{1}^{2-}$ and its stability, calculations were performed at both the MP2/aug-cc-pVDZ and the B3LYP/aug-cc-pVDZ levels of theory (Table 2). The structures were shown to be true minima by calculation of the harmonic vibrational frequencies. The calculations assumed S_6 symmetry for the structure of $\mathbf{1}^{2-}$. When the calculations were repeated starting with C_1 symmetry, they converged to the S_6 structure. Both calculations give structural parameters that are significantly closer to those found in our X-ray study than to those found in ZOMBAE and CHYDNI. The structural parameters obtained from the MP2 calculation match the experimental values reported herein most closely: the Cl−Cl distance differs by only 0.12 Å, the O−O distances by only 0.004 Å, and the Cl−O distances by only 0.058 Å. Similarly, the angles are in excellent agreement, with less than 1° difference. Apparently, ion-pair strain has resulted in a relatively isolated and undistorted $\mathbf{1}^{2-}$ cluster.

Table 2: Structural parameters and standard enthalpies of formation calculated for $[Cl_2(H_2O)_6]^{2-}$ ($\mathbf{1}^{2-}$) and $[Cl(H_2O)_3]^-$ ($\mathbf{2}^-$).

	$[Cl_2(H_2O)_6]^{2-}$ ($\mathbf{1}^{2-}$)			$[Cl(H_2O)_3]^-$ ($\mathbf{2}^-$)	
	X-ray	B3LYP[a]	MP2[b]	B3LYP[a]	MP2[b,c]
Cl−Cl [Å]	6.321	6.554	6.441	–	–
Cl−O [Å]	3.227	3.312	3.285	3.231	3.222
O−O [Å]	2.832	2.869	2.836	3.025	3.009
O-Cl-O [°]	74.55	73.10	73.61	55.82	55.68
O-O-O [°]	87.30	86.85	87.91	60.00	60.00
ΔH^0 [kJ mol^{-1}]	–	−173.3	−222.0	−159.3	−176.7

[a] B3LYP/aug-cc-pVDZ. [b] MP2/aug-cc-pVDZ. [c] Also see reference [12].

Since the corresponding monomer of $\mathbf{1}^{2-}$, $[Cl(H_2O)_3]^-$ ($\mathbf{2}^-$), has been extensively investigated,[2,12] similar calculations were also performed on this cluster for comparison. The Cl−O distances calculated for $\mathbf{1}^{2-}$, which has no net dipole moment, and the polar pyramidal monomer differ by less than 0.07 Å; however, the O−O distances calculated for $\mathbf{1}^{2-}$ are significantly shorter (by 0.18 Å) than those calculated for $\mathbf{2}^-$. This shortening can be attributed to the more favorable O-H-O hydrogen-bonding angle in the O_6H_6 ring of $\mathbf{1}^{2-}$ (171.7°) than in the O_3H_3 ring of $\mathbf{2}^-$ (144.0°). The calculated O-H-Cl angle for $\mathbf{1}^{2-}$ (173.5°) compares more favorably than that for $\mathbf{2}^-$ (179.5°) to the O-H-Cl angle calculated by Xantheas for $[Cl(H_2O)]^-$ (168.0°).[12]

The strongly negative standard enthalpy of formation (ΔH^0) calculated for $\mathbf{1}^{2-}$ attests to its gas-phase stability. Clearly, the six Cl···H−O hydrogen bonds are sufficient to overcome the electrostatic repulsion between the chloride anions. Note that $\mathbf{1}^{2-}$ is not as stable as its monomer $\mathbf{2}^-$ (for comparison, the ΔH^0 for $\mathbf{2}^-$ should be multiplied by 2).[12] This result is not surprising, given the electrostatic repulsion in $\mathbf{1}^{2-}$, even though the hydrogen-bonding interactions may be stronger in the dianion.

In summary, we have described a well-isolated dichloride hydrate cluster in the solid state and have presented the first calculations for such a species, which indicate that it should also be stable in the gas phase. The presence of such dianionic species in hydrated halide phases should, therefore, be considered, particularly in studies involving concentrated solutions and low-polarity environments, even though local polarizations are likely to be important. Spectroscopic studies of $\mathbf{1}^{2-}$ and investigations of other dichloride hydrates remain to be carried out.

Experimental Section

$[C_3(N\mathit{i}Pr_2)_3]Cl{\cdot}3H_2O$ was prepared by addition of $NH\mathit{i}Pr_2$ (20.2 g, 0.200 mol) to C_3Cl_5H (3.28 g, 0.0153 mol) at 0 °C in 1,2-$C_2Cl_2H_4$ (100 mL). The solution was stirred overnight and allowed to warm to ambient temperature. It was then heated under reflux for 2 days. A precipitate of $[NH_2\mathit{i}Pr_2]Cl$ was separated by filtration. The solvent was then removed to give a brown oil, which was washed with aqueous HCl (100 mL) and then water (200 mL). The organic component was extracted with $CHCl_3$, and after solvent removal, a brown crystalline mass entrained in oil remained. Addition of diethyl ether caused the mass to become an oil, from which crystals were obtained upon cooling (0.52 g, 8 % yield). ^{1}H NMR (300 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 3.59$ (septet, ^3J(H,H) = 6.8 Hz, 1 H; $CH(CH_3)_2$), 1.27 ppm (d, ^3J(H,H) = 6.8 Hz, 6 H; $CH(CH_3)_2$). The chemical shift for the water molecules is highly concentration-dependent, but indicative of free water. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 117.6$ (s; C_3), 49.5 (s; $CH(CH_3)_2$), 22.5 ppm (s; $CH(CH_3)_2$). ES-MS (CH_3CN/H_2O, 20 V): m/z (%): 336 (100) $[C_3(NPr_2)_3]^+$, 253 (25) $[C_3(NPr_2)_2OH]^+$. Elemental analysis (%) calcd for $C_{21}H_{48}ClN_3O_3$: C 59.20, H 11.35, N 9.86; found: C 59.53, H 11.25, N 9.71.

X-ray diffraction data for a single crystal of $[C_3(N\mathit{i}Pr_2)_3]Cl{\cdot}3H_2O$ was collected using an APEX II diffractometer equipped with a Bruker SMART CCD area detector. The structure was solved by direct methods and refined by least-squares methods on F^2, with anisotropic thermal parameters for all non-hydrogen atoms. The water hydrogen atoms were refined isotropically with O−H distances of 0.84 Å, and the hydrogen atoms in the O_6H_6 ring were refined with equal distributions over the two possible hydrogen-bonding networks. Crystallographic data and refinement parameters: $C_{21}H_{48}ClN_3O_3$, crystal size 0.85 × 0.26 × 0.18 mm^3, $M_r = 426.07$ g mol^{-1}, triclinic, space group $P\bar{1}$, $a = 9.9248(6)$, $b = 10.1879(6)$, $c = 13.1210(7)$ Å, $\alpha = 82.683(3)$, $\beta = 81.063(3)$, $\gamma = 88.233(3)°$, $V = 1299.84(13)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.089$ g cm^{-3}, $\mu = 0.170$ mm^{-1}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 93(2)$ K, $2\theta_{max} = 69.92°$, 34 404 reflections collected, 10 109 independent reflections ($R_{int} = 0.0310$), $R_1(I \geq 2\sigma(I)) = 0.0342$, $wR_2(I \geq 2\sigma(I)) = 0.0946$, R_1(all) = 0.0427, wR_2(all) = 0.1029, residual electron density = 0.451/−0.209 e Å^{-3}. CCDC-615639 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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