

$[\text{Cl}_2(\text{H}_2\text{O})_6]^{2-}$: Structure of a Discrete Dichloride Hexahydrate Cube as a Tris(diisopropylamino)cyclopropenium Salt**

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Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

The aqueous solvation of halides, chloride in particular, is a highly active area of research since these are among the most common anions in nature, and 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 aqueous salt interfaces, 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 both experimental and theoretical techniques.^[2] Almost all of these studies have focussed on monochloride hydrates of the form $[\text{Cl}(\text{H}_2\text{O})_n]^-$ and have addressed issues such as coordination numbers, the stability and structures of the complexes, their infrared spectra, whether the halides are surface or interior ions etc. Due to the tendency of chlorides to be surface cluster atoms, these clusters invariably have low-energy polar structures.^[2] In contrast to the monochlorides, the study of dihalide hydrates is almost unknown. We are unaware of any theoretical studies on dihalide hydrate clusters and only one brief

structural report of a discrete dichloride hydrate cluster.^[3] Dichloride clusters have a greater potential to form non-polar clusters and, as well as being relevant in concentrated solutions, may be more relevant in hydrophobic and low-polarity environments. We now report on structural and energetic studies of the cubic, dianionic and non-polar cluster $[\text{Cl}_2(\text{H}_2\text{O})_6]^{2-}$ ($\mathbf{1}^{2-}$).

The solid state structure of $[\text{C}_3(\text{N}^i\text{Pr}_2)_3]\text{Cl}\cdot 3\text{H}_2\text{O}$ was initially determined to investigate the effect of anticipated steric interactions between the isopropyl groups in the previously unknown tris(diisopropylamino)cyclopropenium cation. The cation (Figure 1) is interesting in its own right; other amino cyclopropenium cations described to date contain planar N atoms, however, steric interactions force two of the isopropyl groups out of the C_3N_3 plane and one of the N atoms, N2, assumes a distorted tetrahedral geometry in the solid state. The structure of this and related cations will be discussed elsewhere.^[4] To our surprise, the chloride was found as the discrete dichloride hexahydrate cluster, $\mathbf{1}^{2-}$ (Figure 2), with chlorides in opposite corners of a Cl_2O_6 cube. Effectively, each chloride has another chloride 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 is involved in three hydrogen bonds and each O atom has one hydrogen bond with a chloride, one hydrogen bond to an O atom, and one hydrogen bond from another O atom. There are two possible hydrogen-bonding arrangements around the O_6 ring (one is shown in Figure 2) with each arrangement having S_6 symmetry. With the H atom environments averaged, the symmetry becomes D_{3d} . The six O atoms can also be considered to form an O_6 ring in a distorted chair conformation with axial H atoms hydrogen bound to the chlorides. It is also worth noting that the chlorides are not encapsulated by water molecules, but can be considered as examples of surface cluster anions.

There has been one^[3] previous report of such a discrete $\mathbf{1}^{2-}$ cube: Dalley and coworkers reported it as a salt of sodium cryptand [2.2.2] (CCD reference code ZOMBAE).^[5] A dichloride hexahydrate cube with hydrogen bonding to a cationic complex has been characterised (CHYDNI)^[6] and there is also a report of a dibromide hexahydrate cube as part of a hydrogen-bonding network (KIQVAH).^[7] The bromide salt $[\text{K}(\text{Crypt-222})]\text{Br}\cdot 3.5\text{H}_2\text{O}$ has disordered cubes of water molecules and bromide anions as part of a hydrogen-bonding network.^[8] There is also an interesting “inverted” $[\text{Na}_2(\text{H}_2\text{O})_6]^{2+}$ cube within a network of hydrogen bonds.^[9]

Table 1 gives selected distances and angles for $\mathbf{1}^{2-}$ found in our study along with other $[\text{X}_2(\text{H}_2\text{O})_6]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) cubes. The Cl–O distances for the three chloride cubes are quite similar, with the distances in CHYDNI being ca. 0.1 Å shorter than in the other two. The O–O distances in three of the cubes are very similar (2.790–2.888 Å), with those in ZOMBAE being noticeably longer at 3.063 Å. The $[\text{Na}_2(\text{H}_2\text{O})_6]^{2+}$ cube has an average O–O distance of 2.787 Å^[9] and a crystallographically-characterised water cube, $(\text{H}_2\text{O})_8$, also has very similar O–O distances (average of 2.85 Å), although there is considerable variation (2.750–2.929 Å) due to interactions of the

exterior H atoms with the host.^[10] The most obvious 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: the O–Cl–O angles in our structure are ca. 10° degrees smaller than in the other two, while the O–O–O angles are ca. 10° smaller than in CHYDNI, but similar to that in ZOMBAE. The origin of the structural differences between the three $\mathbf{1}^{2-}$ clusters must be a combination of crystal-packing forces in the form of differing electrostatic arrangements and steric interactions, as well as the external hydrogen-bonding interactions in CHYDNI.

As can be seen in Figure 3, we found $\mathbf{1}^{2-}$ to be well isolated from the cationic centers: the chlorides are surrounded by isopropyl groups and the closest interactions of the cluster with the C_3^+ ring occur to O1 and O1' (above and below as shown in Figure 3) with O1–Cl = 3.1488(9) Å, O1–C2 = 3.5190(9) Å and O1–C3 = 3.2460(9) Å. Most of the chloride–cyclopropenium contacts are to methyl groups (there are four methyl carbon atoms at 3.85–4.0 Å: C12, C24, C33 and C25) with the exception of a contact to the H atom on C34, which is alpha to an N 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 ions and the resultant ion-pair strain between the cation and halide which leads to isolated anions.^[11] We might, therefore, expect our cluster to be less distorted from the ideal gas-phase structure than the others, especially CHYDNI since that cluster is involved in external hydrogen bonding.

In order 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 B3LYP/aug-cc-pVDZ level (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 what has been found in ZOMBAE and CHYDNI. As might be expected, the MP2 calculation tends to give structural parameters closest to that reported here. The Cl–Cl distance differs by only 0.12 Å while the O–O distances differ 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 between these parameters. It would seem that ion-pair strain has indeed resulted in a relatively isolated and undistorted $\mathbf{1}^{2-}$ cluster.

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 for $\mathbf{1}^{2-}$, which has no net dipole moment, and its polar pyramidal monomer differ by less than 0.07 Å, however, the O–O distances for $\mathbf{1}^{2-}$ are significantly shorter (by 0.18 Å) than in $\mathbf{2}^-$. This shortening can be attributed to the more favorable hydrogen-bonding angles in the O_6H_6 ring of $\mathbf{1}^{2-}$ (171.7°

versus 144.0° for the O_3H_3 ring in 2^-). The calculated OH–Cl angles of 173.5° in 1^{2-} also compares more favorably than 2^- (179.5°) to that calculated for $[Cl(H_2O)]^-$ (168.0°).^[12] The strongly negative ΔH° calculated for 1^{2-} attests to its gas-phase stability. Clearly, the six Cl–HO hydrogen bonds are sufficient to overcome the electrostatic repulsion between the chlorides. It should be noted, however, that it is not as stable as its monomer 2^- (ΔH° for 2^- should be multiplied by 2 for a more accurate comparison).^[12] This is not surprising given the electrostatic repulsion in 1^{2-} , even though the hydrogen-bonding interactions may be stronger in the dianion.

In summary, we have described an interesting well-isolated dichloride hydrate cluster, presented the first calculations on a dichloride hydrate, and shown that such a species would 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 polarisations are likely to be important. Spectroscopic studies of 1^{2-} and investigations of other dichloride hydrates remain to be carried out.

Experimental Section

$[C_3(N^iPr_2)_3]Cl \cdot 3H_2O$ was prepared by addition of NH^iPr_2 (20.2 g, 0.200 mol) to C_3Cl_5H (3.28 g, 0.0153 mol) at $0^\circ C$ in 1,2- $C_2Cl_2H_4$ (100 mL). The solution was stirred overnight and allowed to reach ambient temperature. It was then heated to reflux for 2 days. A precipitate of $[NH_2^iPr_2]Cl$ was filtered off. The solvent was then removed to give a brown oil which was washed with $HCl(aq)$ (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 diethylether caused the mass to become an oil from which crystals (0.52 g, 8% yield) were obtained upon cooling. 1H NMR (300 MHz, $CDCl_3$, $23^\circ C$, TMS): $\delta=3.59$ (septet, $^3J(H,H)=6.8$ Hz, 1H; $CH(CH_3)_2$), 1.27 ppm (d, $^3J(H,H)=6.8$ Hz, 6H; $CH(CH_3)_2$). The chemical shift for the water is highly concentration dependent but indicative of free water. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, $23^\circ C$, 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 cone voltage): 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 crystallographic data for $[C_3(N^iPr_2)_3]Cl \cdot 3H_2O$ 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 H atoms were refined isotropically with O–H distances of 0.84 Å and the H atoms in the O_6H_6 ring were refined

as equal distributions of the two possible hydrogen-bonding networks. Crystallographic data and refinement parameters: $C_{21}H_{48}ClN_3O_3$, crystal size 0.85x0.26x0.18 mm, $M_r = 426.07 \text{ g mol}^{-1}$, triclinic, space group $P\bar{1}$, $a = 9.9248(6) \text{ \AA}$, $b = 10.1879(6) \text{ \AA}$, $c = 13.1210(7) \text{ \AA}$, $\alpha = 82.683(3)^\circ$, $\beta = 81.063(3)^\circ$, $\gamma = 88.233(3)^\circ$, $V = 1299.84(13) \text{ \AA}^3$, $Z = 2$, $\rho = 1.089 \text{ g cm}^{-3}$, $\mu = 0.170 \text{ mm}^{-1}$, Mo($K\alpha$) radiation ($\lambda = 0.71073 \text{ \AA}$), $T = 93(2) \text{ K}$, $2\theta_{\text{max}} = 69.92^\circ$, 34404 reflections collected, 10109 independent reflections ($R_{\text{int}} = 0.0310$), $R_1(\geq 2\sigma(I)) = 0.0342$, $wR_2(\geq 2\sigma(I)) = 0.0946$, $R_1(\text{all}) = 0.0427$, $wR_2(\text{all}) = 0.1029$, residual electron density = $0.451/-0.209 \text{ e\AA}^{-3}$. The crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 615639. Copies of this information may be obtained on the web at http://www.ccdc.cam.ac.uk/data_request/cif.

- [1] a) H. Ohtaki, T. Radnai, *Chem. Rev.* **1993**, *93*, 1157; b) Y. Marcus, *Ion Solvation*, Wiley, Chichester, **1986**; c) D. T. Richens, *The Chemistry of Aqua Ions*, Wiley, Chichester, **1997**.
- [2] Some recent leading references: a) D. D. Kemp, M. S. Gordon, *J. Phys. Chem. A* **2005**, *109*, 7688; b) W. H. Robertson, M. A. Johnson, *Ann. Rev. Phys. Chem.* **2003**, *54*, 173; c) R. Ayala, J. M. Martínez, R. R. Pappalardo, E. S. Marcos, *J. Chem. Phys.* **2003**, *119*, 9538; d) R. Custelcean, M. G. Gorbunova, *J. Am. Chem. Soc.* **2005**, *127*, 16362; e) P.S. Lakshminarayanan, E. Suresh, P. Ghosh, *Angew. Chem.* **2006**, *118*, 3891; *Angew. Chem. Int. Ed.* **2006**, *45*, 3807.
- [3] It should be noted that searching for hydrogen-bonding motifs can be fraught with difficulties: M. Mascali, L. Infantes, J. Chisholm, *Angew. Chem.* **2006**, *118*, 36; *Angew. Chem. Int. Ed.* **2006**, *45*, 32.
- [4] J. R. Butchard, O. J. Curnow, D. J. Garrett, manuscript in preparation.
- [5] N. K. Dalley, K. E. Krakowiak, J. S. Bradshaw, X. Kou, R. M. Izatt, *J. Heterocyclic Chem.* **1995**, *32*, 1201.
- [6] K. F. Belyaeva, V. N. Biyushkin, V. A. Neverov, L. A. Nezhel'skaya, N. I. Belichuk, T. I. Rozhdestvenskaya, *Koord. Khim.* **1981**, *7*, 433.
- [7] J. Springborg, B. Nielsen, C. E. Olsen, I. Søjtofte, *J. Chem. Soc., Perkin Trans. 2* **1999**, 2701.
- [8] A. N. Chekhlov, *Russ. J. Coord. Chem.* **2005**, *31*, 230.

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- [9] C. Chulvi, M. C. Munoz, L. Perello, R. Ortiz, M. I. Arriortua, J. Via, K. Urriaga, J. M. Amigo, L. C. Ochando, *J. Inorg. Biochem.* **1991**, *42*, 133.
- [10] W. B. Blanton, S. W. Gordon-Wylie, G. R. Clark, K. D. Jordan, J. T. Wood, U. Geiser, T. J. Collins, *J. Am. Chem. Soc.* **1999**, *121*, 3551.
- [11] R. Weiss, T. Brenner, F. Hampel, A. Wolski, *Angew. Chem.* **1995**, *107*, 481; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 439.
- [12] S. S. Xantheas, *J. Phys. Chem.* **1996**, *100*, 9703.

Legends for Figures

Figure 1. Thermal ellipsoid plot of the cation in $[\text{C}_3(\text{N}^i\text{Pr}_2)_3]\text{Cl}\cdot 3\text{H}_2\text{O}$. Hydrogen atoms have been omitted for clarity. Selected 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).

Figure 2. Thermal ellipsoid plot of the anionic cluster in $[\text{C}_3(\text{N}^i\text{Pr}_2)_3]\text{Cl}\cdot 3\text{H}_2\text{O}$ illustrating one of the hydrogen-bonding arrangements. Selected 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).

Figure 3. Two orthogonal views that illustrate the environment around the $[\text{Cl}_2(\text{H}_2\text{O})_6]^{2-}$ cluster (Cl, green; O, red; N, blue; C, black).

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

	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

Table 2. Structural parameters and standard enthalpies for the formation of $[Cl_2(H_2O)_6]^{2-}$ and $[Cl(H_2O)_3]^-$ from Cl⁻ and H₂O calculated at the B3LYP/aug-cc-pVDZ and MP2/aug-cc-pVDZ levels.

	$[Cl_2(H_2O)_6]^{2-}$			$[Cl(H_2O)_3]^-$	
	X-ray	B3LYP	MP2	B3LYP	MP2 ^[a]
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° [kJmol ⁻¹]	–	–173.3	–222.0	–159.3	–176.7

[a] Also see reference 12.

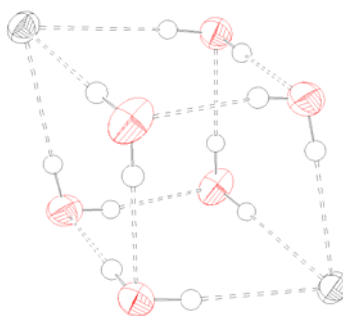
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Chloride hydrate clusters

James R. Butchard, Owen J. Curnow,* David J. Garrett, Robert G. A. R. Maclagan

$[\text{Cl}_2(\text{H}_2\text{O})_6]^{2-}$: Structure of a Discrete Dichloride Hexahydrate Cube as a Tris(diisopropylamino)cyclopropenium Salt

Chlorides can be glued together: Six Cl–HO hydrogen bonds are sufficient to provide the glue to overcome the electrostatic repulsion between two chlorides and give a stable dichloride hydrate. An X-ray structural study is consistent with a gas-phase calculated structure.



Keywords: chloride · cluster compounds · hydrates · hydrogen bonds · water

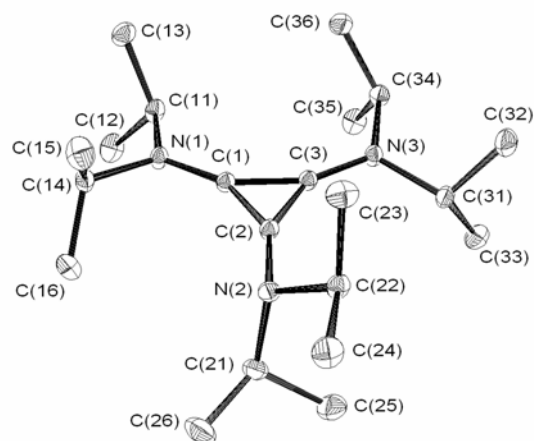


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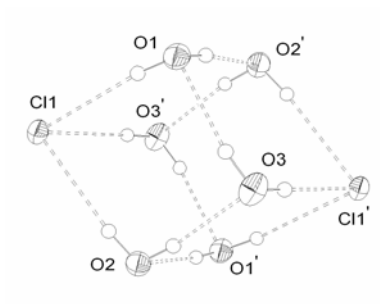


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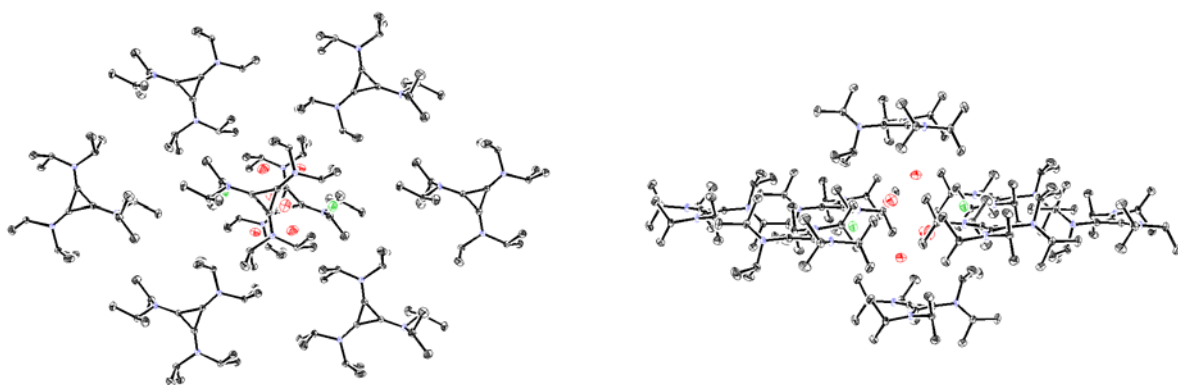


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