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A Discrete Dichloride Tetrahydrate Trapped by a Cyclopropenium Cation: Its Structure and Spectroscopic Properties

Mohammed S. Abdelbassit,^[a] Owen J. Curnow,*^[a] Manuel Ferreras^[a] and Deborah L. Crittenden*^[a]

Abstract: A discrete dichloride tetrahydrate cluster, $[Cl_2(H_2O)_4]^{2-}$, was obtained as a salt of the bis(diphenylamino)diethylamino cyclopropenium cation $[C_3(NPh_2)_2(NEt_2)]^+$ and characterized by single crystal X-ray diffraction and infrared spectroscopy. This chloride-chloride ion-pair cluster consists of a $[Cl_2(H_2O)_2]^{2-}$ square with opposite edges bridged by water molecules to give a chair-like structure of the non-hydrogen atoms. The solid state structure is essentially the same as the calculated gas-phase structure. Infrared spectra were also collected on the deuterium analogue $[Cl_2(D_2O)_4]^{2-}$. Computational studies were carried out on gas-phase $[Cl_2(H_2O)_4]^{2-}$ to confirm the infrared band assignments in the solid state. The structure and infrared spectrum are consistent with the discrete nature of the cluster.

Introduction

Chloride-water clusters are fundamentally-important motifs for understanding a wide range of physicochemical processes in nature. For example, they play a vital role in biological and geological systems; particularly at water/membrane interfaces and in the mobility of ions through ion channels, as well as in electrical phenomena in the troposphere and ionosphere.^[1] Indeed, there are extensive theoretical studies on monochloride hydrate [Cl(H₂O)_n]⁻ clusters over the last several years.^[2,3] On the other hand, there are only five reported ab initio studies on dichloride hydrates [Cl₂(H₂O)_n]^{2-,[4–7]} Despite the expected ion-ion repulsion between chloride ions, there is strong evidence for the formation of Cl⁻---Cl⁻ ion pairs in aqueous solution, particularly in concentrated solutions.^[4,5,8]

In 2013, Basu et al. synthesized the simplest hydrated dichloride cluster found to date, $[Cl_2(H_2O)_2]^2$, by using an amide receptor. The Cl⁻ anions are bridged by two H₂O molecules, and the structure is stabilized by additional hydrogen bonds (two NH---OH₂ and two NH---Cl⁻).^[9] $[Cl_2(H_2O)_2]^{2-}$ was also reported by Szumna et al. in 2001 as a co-crystal of a neutral octalactam receptor with tetrabutylammonium chloride. The $[Cl_2(H_2O)_2]^{2-}$ cluster lies in a monocyclic cavity held via eight hydrogen bonds (four NH---OH₂ and four NH---Cl⁻). There is also hydrogen

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bonding between the Cl⁻ and dichloromethane in the extended lattice.^[10] In 2012, Wang et al. prepared a discrete $[Cl_2(H_2O)_2]^{2-}$ structure; although it exhibits strong Cl⁻– π and H₂O– π interactions with electron-deficient regions of the triazine rings.^[11] Furthermore, Safin et al. claimed a discrete structure of dichloride dihydrate, however, the cluster is in fact supported by four amino-NH hydrogen bonds with H₂O and Cl⁻.^[12] We do not believe that a cluster held together by hydrogen bonding should be described as "discrete" when ignoring additional strong hydrogen bonds to the cluster fragment.

To the best of our knowledge there are only three solid-state structures of the tetrahydrate $[Cl_2(H_2O)_4]^{2-}$ that have been reported. The first one has prepared as the counterion of a nickel(II) complex and is attached to the ligands through six NH---Cl⁻ and four NH---OH₂ hydrogen bonds.^[13] The second structure, reported by Arunachalam and Ghosh, was formed in two bowlshaped tripodal receptors in an octahedral-like arrangement in which all of the water molecules are disordered over two positions and which consequently defies a reasonable structural description. The structure is stabilized by multiple amide -NH hydrogen bonding with Cl⁻ and H_2O .^[14] The third structure was reported by Chakraborty et al. in 2014 as a tetrabutylammonium salt; the hydrated cluster is encapsulated in a pyridylfunctionalized receptor. Nevertheless, the structure shows strong hydrogen bonding between the cluster and the receptor.^[15] We have previously reported the structure of a discrete dichloride hexahydrate $[Cl_2(H_2O)_6]^{2-}$ cube with the triaminocyclopropenium (TAC) cation [C₃(N^{*i*}Pr₂)₃]^{+.[6]} The larger dichloride-water aggregates $[Cl_2(H_2O)_8]^{2-[16]}$ and $[Cl_2(H_2O)_{14}]^{2-[17]}$ have been investigated in supramolecular systems as part of hydrogenbonding networks. The decahydrate [Cl₂(H₂O)₁₀]²⁻ has been obtained as one unit, but with strong hydrogen bonding to two adjacent Na⁺-water clusters.^[18] Unfortunately, the vibrational modes were not reported for any of these clusters due to overlapping with the bands of the NH groups, except for the dichloride hexahydrate.^[6] The vibrational modes of a limited number of monochloride hydrates have been observed via Artagging at low temperature in the gas phase.^[3]

Herein, we present a new hydrophobic environment, $[C_3(NPh_2)_2(NEt_2)]^{+}$, to host a discrete dichloride tetrahydrate cluster. The crystal structure and the spectroscopic properties (FT-IR) of $[Cl_2(H_2O)_4]^{2-}$ and the $[Cl_2(D_2O)_4]^{2-}$ analogue, as well as a theoretical study, will be discussed.

Results and Discussion

Synthesis

We synthesized the new TAC cation diethylaminobis(diphenylamino)cyclopropenium, $[C_3(NPh_2)_2(NEt_2)]^+$, as a

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chloride salt via the addition of a mixture of HNPh₂ and NEt₃ (3 : 4.5 molar ratio) to one equivalent of pentachlorocyclopropane (Scheme 1). Four cations were obtained: the ammonium salts $[H_2NPh_2]CI$ and $[HNEt_3]CI$ along with two TAC-based salts $[C_3(NEt_2)_2(NPh_2)]CI$ and $[C_3(NPh_2)_2(NEt_2)]CI$, from which the latter was ultimately isolated as a dihydrate in 41% yield. The crystallization was carried out in a water-saturated binary solvent of dichloromethane and ethyl acetate (1:1 v/v) at room temperature. The $[Cl_2(D_2O)_4]^{2-}$ analogue was prepared by evaporation of a D₂O-saturated dichloromethane solution.



Scheme 1. Synthesis of [C₃(NPh₂)₂(NEt₂)]Cl.

Single crystal structure

 $[C_3(NPh_2)_2(NEt_2)]CI.2H_2O$ crystallizes in the triclinic space group *P-1* (Table 1) in which the asymmetric unit consists of one cation and a chloride dihydrate. In the cation, the phenyl groups exhibit a propeller conformation to minimize the steric interactions (Figure 1).



Figure 1. The geometry and labeling scheme of the cation in $[C_3(NPh_2)_2(NEt_2)]Cl\cdot 2H_2O$. Hydrogen atoms are omitted for clarity.



$\label{eq:constraint} \begin{array}{llllllllllllllllllllllllllllllllllll$	refinement data for
formula	C31H34CIN3O2
a [Å]	8.9507(3)
b[Å]	11.4993(3)
c [Å]	14.6291(4)
α [°]	68.871(3)
β [°]	79.571(2)
γ [°]	89.225(2)
V [Å ³]	1379.10(7)
Z	2
$ ho_{\text{calc}}$ [g cm ⁻³]	1.243
crystal system	triclinic
space group	<i>P</i> -1
shape/colour	colourless
crystal size [mm]	0.299 × 0.243 × 0.113
μ [mm ⁻¹]	1.476
<i>T</i> [K]	120(10)
F(000)	548
2θ range [°]	8.256 – 147.114
index ranges	–11 ≤ <i>h</i> ≤ 11
	–13 ≤ <i>k</i> ≤ 14
	–18 ≤ / ≤ 18
reflections collected	28951
independent reflns	5536
R(int)	0.0304
data/restraints/parameters	5536/2/346
GoF on F ²	1.063
R_1/wR_2 [$l>2\sigma(l)$]	0.0429/0.1181
R_1/wR_2 (all data)	0.0469/0.1215
$\Delta \rho_{\text{max/min}}/\text{e} [\text{Å}^{-3}]$	1.19/0.47

The structural parameters for the cation are given in the supplementary material. Bond distances indicate that the π donation into the C₃ ring from the diethylamino group is enhanced by the presence of the electronegative phenyl groups. The extended lattice shows that the cations form a short contact through the phenyl groups (C36'---C36") of 3.135(3) Å (Figure 2), which is found to be shorter than most " π -stacked" neutral arenes at 3.3–3.8 Å.^[19] This strong interaction can be attributed to the substituent effects on the π -stacking geometry and thus the formation of benzene dimers.^[20]

The chloride dihydrate forms a C_i -symmetric dimeric structure of $[Cl_2(H_2O)_4]^{2-}$ which can be described as having a square $[Cl_2(H_2O)_2]^{2-}$ core with two additional terminal H_2O bridging molecules on opposite Cl---O edges. Folding about the bridged edges produces a chair-like conformation (Figure 3).



Figure 2. Edge-to-edge π -stacking between two cations in $[C_3(NPh_2)_2(NEt_2)]Cl\cdot 2H_2O$, C36'---C36" 3.135(3) Å. Hydrogen atoms are omitted for clarity.

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Table 2. Structural parameters for $[X_2(H_2O)_4]^{2-}$ (X = F, Cl) clusters.							
Parameter	X-ray	Calculated best estimate ^[a]	Calculated range ^[b]	HIMJUJ ^[13]	CIVGAR ^[15]	CIVGEV ^[15]	
х	CI	CI	CI	CI	CI	F	
0102 [Å]	3.116(3)	2.92	2.71 – 3.11	2.707(11)	4.456(3)	4.0067(7)	
X–X [Å]	5.0932(8)	5.50	5.09 – 5.97	5.175(4)	4.317(13)	3.961(5)	
X1O1 [Å]	3.191(2)	3.29	3.17 – 3.44	4.015(6)	3.251(2)	2.647(7)	
X1O2 [Å]	3.2900(16)	3.34	3.14 – 3.62	3.172(6)	3.375(3)	2.702(5)	
X1AO2 [Å]	3.2250(17)	3.34	3.13 – 3.59	3.157(8)	3.317(3)	2.618(6)	
X1–O2–X1A [°]	102.84(5)	110.9		109.7(2)	82.97(6)	97.21(17)	
02–X1–O2A [°]	77.16(5)	69.1	-	70.3(2)	97.03(6)	83.79(17)	
O1–X1–O2 [°]	57.46(5)	52.2		42.24(18)	88.45(7)	99.1(2)	
02–01–X1 [°]	62.86(5)	64.8	-	52.00(16)	44.72(5)	40.19(12)	
O1–O2–X1 [°]	59.68(5)	63.0	-	85.8(2)	46.82(5)	40.73(14)	
Fold angle [°]	29.38(7)	50.3	-	40.4(3)	17.41(6)	60.6(2)	

^[a] MP2/aug-cc-pVDZ, ^[b] LDA/pc-2 and HF/pc-2 values provide conservative lower and upper bounds for predicted interatomic distances.^[21]



Figure 3. The structure of $[Cl_2(H_2O)_4]^{2-}$ in $[C_3(NPh_2)_2(NEt_2)]Cl\cdot 2H_2O$. Dashed lines indicate hydrogen bonds. The computationally optimized gas phase structure is visually indistinguishable.

Figure 4 depicts the environment around the $[Cl_2(H_2O)_4]^{2-}$ cluster. The cluster is sandwiched between two cyclopropenium cations and supported by another two cations via weak hydrogen bonds (C---O ~3.4 Å) between the water molecules within the cluster and neighbouring aryl and methyl substituents (see Figure 1S for detailed illustration). Notably, the chloride anions are located even further away from the centers of the cyclopropenium rings (Cl---C₃ = 3.48 Å). Each chloride anion engages in six hydrogen bonds; three of them are strong Cl---HO hydrogen bonds within the cluster (3.19 – 3.29 Å) and three are weak Cl---HC aryl hydrogen bonds to the surrounding cations (3.64 – 3.67 Å). This contrast between strong intra-cluster hydrogen bonding and weak interactions with the surrounding cyclopropenium units provides strong evidence for the existence of a discrete dichloride tetrahydrate structure within the crystalline environment.

If the cluster we have identified is truly discrete, then it should be stable or at least semi-stable in the gas phase. To the best of our knowledge, no direct experimental evidence for gas phase

 $[Cl_2(H_2O)_4]^{2-}$ clusters is available to date, but there is strong computational evidence that such clusters can exist in thermodynamically stable forms in the gas phase.^[5,7] However, previous studies have either failed to identify the Ci-symmetric cluster as a local minimum,^[7] or omit pertinent structural and spectroscopic data for this particular conformation.^[5] Although previous studies indicate that the Ci-symmetric cluster is not the global minimum in the gas phase, it is reasonable to expect that the greater symmetry of the C_i cluster would be favoured during crystal formation over the C1-symmetric extended bridged structures that would otherwise form to minimize ion-ion repulsion in the gas phas. Ivanov et al. calculated that a C_1 structure with a chain of three waters between the chlorides has the lowestenergy gas-phase structure by 5.7 kcal/mol (CCSD(T)/aug-ccpVDZ) compared to the C_i structure, whereas a D_{4h} -symmetric structure with four bridging waters is 9.6 kcal/mol higher in energy than the C1 structure.^[5] Here we report predicted structural parameters for the Ci-symmetric cluster in Table 2, along with conservative computational error estimates for the interatomic distance parameters. For reference, structural parameters for other crystallographically-characterized $[Cl_2(H_2O)_4]^{2-}$ and $[F_2(H_2O)_4]^{2-}$ non-discrete clusters have also been extracted from the literature data.[13,15]

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Figure 4. The environment of $[Cl_2(H_2O)_4]^{2-}$ in $[C_3(NPh_2)_2(NEt_2)]Cl.2H_2O$ Hydrogen atoms are omitted for clarity.

Direct comparison of computed and observed structural parameters is not generally straightforward, because differences between them can be attributed to a combination of physical effects (crystal packing, thermal and zero-point vibrational motion) and computational artefacts (errors associated with choice of electronic structure method and basis set incompleteness) that cannot be disentangled. Nonetheless, it is clear that only the $[Cl_2(H_2O)_4]^{2-}$ structure reported here resembles its gas phase counterpart, according to the parameters reported in Table 2. For all intra-cluster distances, our observed values fall within the computed upper and lower bounds, although they are not in perfect agreement with the best computational estimates. This implies that crystal packing and nuclear vibrational effects are of approximately the same magnitude as computational method uncertainties.

Table 3. Experimental and calculated anharmonic vibrational frequencies (in cm^-1) for $[Cl_2(H_2O)_4]^{2-}$ and $[Cl_2(D_2O)_4]^{2-}$

Solid-state experimental	Gas phase calculated ^[a]	Deuterated experimental	Assignment
3632	3541	2677	v(asym, syn)
-	3516	-	v(asym, anti)
3470	3460	2583	v(sym, outer)
3405	3409	2504	v(sym, inner)
3310	3357	2453	2v(bend, outer)
3250	3192	2394	2v(bend, inner)
1655	1679	1225	v(bend, outer)
1625	1596	1198	v(bend, inner)

^[a] Frequencies computed at MP2/aug-cc-pVDZ with empirical anharmonic correction applied.

Comparison with other literature structures reveals that much larger differences are observed if the cluster forms additional bonds with surrounding molecules. Kopylovich et al. synthesized similar structures of a hexameric water cluster $(H_2O)_6$ and a dichloride tetrahydrate $[Cl_2(H_2O)_4]^{2-}$ (CSD reference code HIMJUJ), which contain a square core of $(H_2O)_4$ and $[Cl_2(H_2O)_2]^{2-}$, respectively, with two additional H₂O molecules.^[13] Their structure is similar to the one reported here, and consistent with gas phase computational data except for the extended Cl--O1 distance of 4.02 Å, which arises from the fact that the terminal or "outer" water does not form a hydrogen bond back to chloride but instead hydrogen bonds to a neighbouring pyridine ring (N--O = 2.81 Å).

Chakraborty et al. reported the structures $[Cl_2(H_2O)_4]^{2-}$ (CIVGAR) and $[F_2(H_2O)_4]^{2-}$ (CIVGEV),^[15] but these clusters are even less discrete than those reported by Kopylovich et al. Both are stabilized by strong (amide)-NH hydrogen bonding from the receptor to CI⁻ and H₂O. Notably, the terminal water molecules hydrogen bond to both the pyridine ring in the receptor and the chloride ions, which prevents them interacting with the central water molecules (O---O = 4.46 Å).

Further evidence that our crystallographically-trapped cluster resembles its gas phase counterpart lies in the close agreement between computed and observed intermolecular bonding angles, which agree to within 10° for our system but differ substantially in others.

At first glance, the $\sim 20^{\circ}$ difference between fold angles that the terminal water molecule subtends to the central dichloride dihydrate square appears to contradict the otherwise close agreement between computed gas phase structural parameters and their experimentally observed X-ray structure counterparts. However, this hinge angle is particularly soft and therefore can be easily influenced by crystal-packing effects.

Infrared spectroscopy

Vibrational spectroscopy provides detailed information about bonding within and around solvated ion complexes,^[22] and therefore is an ideal technique to probe the discreteness of the dichloride tetrahydrate captured here.

Mid-IR spectra were recorded for [C₃(NPh₂)₂(NEt₂)]Cl.2H₂O and its deuterated analogue [C₃(NPh₂)₂(NEt₂)]Cl.2D₂O, and subtracted from one another to suppress bands arising from the cyclopropenium units and isolate peaks arising from the dichloride tetrahydrate clusters. The stretching region of the resultant difference spectrum is illustrated in Figure 5, superimposed with computationally predicted line spectra illustrating both predicted band centres and relative intensities. The band patterns for the isotopomers are identical, but shifted due to isotopic mass effects. Experimental and computational band centres are reported in Table 3. Analysis of the bending region reveals two bending bands - a strong band at 1625 cm⁻¹ (1198 cm⁻¹ for deuterated isotopologue) and a much weaker band at 1655 cm⁻¹ (1225 cm⁻¹ for deuterated isotopologue). This immediately helps identify and assign the peaks at 3250 cm⁻¹ and 3310 cm⁻¹ as bending overtones. Although these bands formally have zero intensity in harmonic frequency calculations, their predicted positions are indicated by dots at appropriate positions along the x axis.

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To make further progress in assigning the observed spectrum, we turn to the computational results reported in Table 3 and illustrated in Figure 6. A pair of high frequency asymmetric stretching modes separated by ~ 20 cm⁻¹ are expected, but only one is observed. It is assigned to the fundamental stretching mode that undergoes the largest change in dipole moment; v(asym, syn). It is most likely that the nearby lower-intensity v(asym, anti) fundamental is simply subsumed into the band centred at 3632 cm⁻¹.

The two symmetric stretching fundamentals at 3470 cm^{-1} and 3405 cm^{-1} are easy to identify and assign, because the experimental band centres align closely with their computationally-predicted values.

The highest intensity bending mode corresponds to the inphase bending of the two "inner" water molecules within the square planar dichloride dihydrate core. Both the fundamental and overtone bands are clearly visible in the difference spectrum at 1625 and 3250 cm⁻¹, respectively. Bending of the outer water molecules causes a much smaller change in dipole moment of the dichloride tetrahydrate cluster as a whole, so the v(bend, outer) fundamental has a much lower transition intensity and is observed as a very weak band at 1655 cm⁻¹. Its overtone is barely visible and only shows up as a very weak shoulder at 3310 cm⁻¹.

A few small discrepancies between theory and experimental exist; v(bend, outer) appears to be slightly overestimated by all computational approaches employed here and v(asym, syn) underestimated. Unlike for the structural parameters, we have not attempted to provide bounds for the predicted anharmonic frequencies, so it is certainly plausible that these remaining discrepancies are computational artefacts. However, it is also possible that crystal packing and thermal effects that we have not attempted to account for here could account for the residual differences between computational predictions and experimental observations.



Figure 6. Fundamental stretching and bending vibrational modes of dichloride tetrahydrate.

In either case, the differences are small, and inconsequential. The close agreement between computationally-predicted anharmonic gas phase transition frequencies and observed solid state IR band centres provides strong evidence that we have isolated a discrete dichloride tetrahydrate structure, encapsulated predominantly through steric confinement, i.e. exhibiting only weak interactions with its surrounding environment.

Conclusions

We have illustrated the first example of a discrete dichloride tetrahydrate, $[Cl_2(H_2O)_4]^{2-}$, in the solid-state by taking advantage of the weak interactions between anions and triamino-cyclopropenium cations. The vibrational modes of a discrete chloride hydrate species have been observed and assigned for the first time in the solid state. In addition, we have also reported the optimized structure and the calculated IR-active vibrational frequencies of $[Cl_2(H_2O)_4]^{2-}$ in the gas-phase which are in excellent agreement with the solid state structure and the experimental infrared spectrum.

Experimental Section

All the experimental work and sample preparation were carried out under dried nitrogen atmosphere using standard Schlenk techniques. CH_2Cl_2 , diethylether, ethylacetate, D_2O , triethylamine and diphenylamine were obtained commercially. Solvents were dried using an in-house solvent purification system.

TGA/DSC data were collected on dried samples using a TA Instruments SDT Q600 at 10 °C min⁻¹. Mid-IR data were collected at room temperature by using a Vertex 70 FT-IR spectrometer from Bruker (Germany), operating with a Platinum ATR unit with a diamond crystal. A resolution of 4 cm⁻¹ and 16 scans were taken. Microanalyses were performed by Campbell Microanalytical Laboratory, University of Otago, Dunedin.

Diethylaminobis(diphenylamino)cyclopropenium chloride dihydrate $[C_3(NPh_2)_2(NEt_2)]Cl.2H_2O$

A solution of HNPh₂ (9.87 g, 58.37 mmol) and NEt₃ (12.2 mL, 87.56 mmol) in CH₂Cl₂ (75 mL) was added slowly to a solution of C_3Cl_5H (4.14 g, 19.46 mmol) in CH₂Cl₂ (50 mL) and cooled to 0 °C. After stirring for 1h, the reaction mixture was stirred overnight at ambient temperature. CH₂Cl₂ was removed *in vacuo* to give a dark-brown liquid. ES-MS shows the presence of [HNEt₃]⁺, [H₂NPh₂]⁺, [C₃(NEt₂)₂(NPh₂)]⁺ and [C₃(NPh₂)₂(NEt₂)]⁺. [HNEt₃]Cl was filtered off after precipitation by the addition of acetone (75 mL). [H₂NPh₂]Cl and [C₃(NEt₂)₂(NPh₂)]Cl salts were separated by column

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chromatography using silica-gel 60G and CH₂Cl₂-ethylacetate (1:1 v/v) as the mobile phase. Ethanol was then used to elute [C₃(NPh₂)₂(NEt₂)]Cl and the solvent was removed *in vacuo* to give a pale yellow solid. Undried CH₂Cl₂-ethylacetate (1:1 v/v) was used for crystallization, and slow evaporation at ambient temperature gave pale yellow plates (3.54 g, Yield 41%).¹H NMR (400 MHz, CD₃CN): δ = 0.88 (t, ³*J*(H,H) = 7.04 Hz, 2H; NCH₂CH₃), 2.76 (q, ³*J*(H,H) = 7.04 Hz, 3H; NCH₂CH₃), 7.16-7.34 ppm (m, 10H; NC₆H₅). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 13.54 (NCH₂CH₃), 46.77 (NCH₂CH₃), 122.31, 124.30 (C₃) ring, 114.47, 127.22, 129.66, 142.83 (NC₆H₅). EI-MS: Found m/z 445.2490 [M⁺]; Calcd 445.2490 [M⁺]. C₃₁H₃₄N₃ClO₂: C, 72.70; H, 6.65; N, 8.14; Found: C, 73.08; H, 6.46; N, 8.13.

Crystal data

A suitable crystal was mounted on a SuperNova, Dual, Mo at zero, Atlas diffractometer. Using Olex2,^[23] the structure was solved with the XS structure solution program^[24] using Direct Methods and refined with the XL refinement package^[24] using Least Squares minimisation with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms on the methylene groups were refined isotropically at their calculated positions and methyl groups were refined as rotating groups. The water protons were located from the density difference map and refined isotropically. CCDC-1981447 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Computational

Geometries of gas-phase $[Cl_2(H_2O)_4]^{2-}$ clusters were optimised at HF/pc-2, HFS/pc-2, and MP2/aug-cc-pVDZ, and harmonic vibrational frequencies computed at MP2/aug-cc-pVDZ. An empirical quadratic correction model was applied to obtain predicted anharmonic vibrational frequencies.^[25] All *ab initio* calculations were performed using the NWChem program package.^[26]

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Keywords: dichloride • hydrate • infrared • solvate • X-ray diffraction

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A discrete dichloride tetrahydrate trapped in a hydrophobic environment

FULL PAPER

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triaminocyclopropenium А phenyl-based cation crystallizes with a discrete dichloride tetrahydrate cluster. The structure and infrared spectrum agree well with gas-phase calculations, and thus confirm the discreteness of the cluster. It can be viewed as a chloride-chloride ion pair bridged by two waters to form a square, with two additional waters added across opposite edges to give an overall structure with a chairlike conformation.

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