structure solution and refinement. The data were corrected for Lorentz-polarization effects during the final stages of data reduction.

**Solution and Refinement of the Structure of Complex 2.** Solution of the structure was straightforward from application of the heavy-atom method. Space group *Pbca* was confirmed and the position of the iron atom was deduced from the three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations.

Least-squares refinement[29] of the 35 non-hydrogen atoms, varying the iron atom anisotropically, produced unweighted and weighted residuals of 8.7% and 7.1%,[30] respectively. Hydrogen atom positions were calculated by using a C-H distance of 0.95 Å and an isotropic thermal parameter of 6.0 Å$^2$. Further refinement resulted in residuals of $R = 7.2\%$ and $R_w = 5.5\%$. The final difference Fourier map had no peak greater than 0.26 e/Å$^3$.

**Acknowledgment** is made to the National Institutes of Health (GM 28938) and the Department of Energy, Office of Basic Energy Sciences (85ER 13430), for support of this work.

**Supplementary Material Available:** Tables of complete anisotropic and isotropic temperature factors, bond distances and angles, calculated hydrogen positions, and defined planes and calculated dihedral angles for **2** (3 pages); a table of calculated and observed structure factors for **2** (10 pages). Ordering information is given on any current masthead page.

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(29) The function minimized was $\sum w(|F_o| - |F_c|)^2$.

(30) $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

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# Synthesis of Salts of the Hydrogen Dichloride Anion in Aromatic Solvents. 2. Syntheses and Crystal Structures of [K·18-crown-6][Cl-H-Cl], [Mg·18-crown-6][Cl-H-Cl]$_2$, [$H_3O$·18-crown-6][Cl-H-Cl], and the Related [$H_3O$·18-crown-6][Br-H-Br]

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The reaction of HCl(g), $H_2O$, and 18-crown-6 in toluene gives [$H_3O$·18-crown-6][Cl-H-Cl]·3.6tol (tol = toluene), from which crystals of [$H_3O$·18-crown-6][Cl-H-Cl] are isolated: space group $P2_1/c$; $a = 10.475$ (7), $b = 20.767$ (9), $c = 8.583$ (7) Å; $\beta = 96.23$ (3)°; $Z = 4$ for $D_c = 1.28$ g cm$^{-3}$; $R = 0.042$ for 493 independent observed reflections. The liquid clathrate [$H_3O$·18-crown-6][Cl-H-Cl]·3.6tol dissolves KCl, and upon standing, the solution affords crystals of [K·18-crown-6][Cl-H-Cl]: space group $P2_1/c$; $a = 8.325$ (2), $b = 14.094$ (4), $c = 7.893$ (6) Å; $\beta = 98.56$ (4)°; $Z = 2$ for $D_c = 1.37$ g cm$^{-3}$; $R = 0.055$ for 1194 independent observed reflections. In a similar fashion, the liquid clathrate dissolves $MgCl_2$ and yields [Mg·18-crown-6][Cl-H-Cl]$_2$: space group *Pbca*; $a = 18.310$ (7), $b = 7.512$ (6), $c = 29.085$ (8) Å; $Z = 8$ for $D_c = 1.44$ g cm$^{-3}$; $R = 0.066$ for 1204 observed reflections. The [Br-H-Br]$^-$ anion is produced by the reaction of HBr(g), $H_2O$, and 18-crown-6 in toluene. [$H_3O$·18-crown-6][Br-H-Br] is isomorphous with the [Cl-H-Cl]$^-$ analogue, and the crystals belong to space group $P2_1/c$ with $a = 10.588$ (1) Å, $b = 21.060$ (2) Å, $c = 8.753$ (1) Å, $\beta = 95.25$ (4)°, and $D_c = 1.52$ g cm$^{-3}$ for $Z = 4$; $R = 0.059$ for 1697 observed reflections. The Cl···Cl separations range from 3.11 (1) Å in the $H_3O^+$ salt to 3.331 (2) Å in the $Mg^{2+}$ analogue. The angle at the hydrogen atom in the hydrogen dichloride ranges from 161° for the [Mg·18-crown-6]$^{2+}$ salt to 180° for the [K·18-crown-6]$^+$ salt. The short Cl···Cl separations in the $H_3O^+$ and $K^+$ salts are attributed to the absence of a strong directional interaction of the anion with the cation. For the long Cl···Cl in the $Mg^{2+}$ case, the magnesium atom is bonded to one of the chlorine atoms at 2.428 (6) and 2.454 (3) Å (two independent anions). The Br···Br distance in [$H_3O^+$·18-crown-6][Br-H-Br] is 3.377 (1) Å.

## Introduction

The hydrogen dichloride ion, Cl-H-Cl$^-$, was first inferred by Kaufler and Kunz[1] in 1909 in the reaction

$$\mathrm{HNR_3Cl + HCl \rightarrow [HNR_3][Cl\text{-}H\text{-}Cl]} \qquad (1)$$

More recently, salts containing the hydrogen dichloride ion were prepared by the reaction of an alkali-metal chloride with HCl in aqueous media[2] or by the reaction of phosphonium halides or phosphanes with hydrogen chloride.[3]

In an effort to convert O- and N-containing bases into salts that might exhibit the liquid clathrate effect,[4] our group has begun a thorough investigation of the interaction of HCl(g) with these bases in aromatic solvents. The first communication in this series[5] involved the reaction with 18-crown-6 according to eq 2. Here

$$\mathrm{18\text{-}crown\text{-}6 + H_2O + HCl(g) \xrightarrow{toluene} [H_3O{\cdot}18\text{-}crown\text{-}6][Cl\text{-}H\text{-}Cl]} \qquad (2)$$

we show that a range of hydrogen dichloride salts are available from a similar synthetic approach, and we present the crystal structures of three examples. In addition, a related salt of hydrogen dibromide is reported.

## Experimental Section

**Materials.** Anhydrous HCl(g) and HBr(g) were purchased from Airco and were further dried by passage through two $H_2SO_4$ traps immediately before use. The $H_2O$ was distilled. KCl, $MgCl_2$, and KBr were analytical reagent grade and were used without additional purification. 18-crown-6 was purchased from Aldrich and was dried under vacuum at 105 °C. The toluene and benzene were dried in the usual manner and distilled under nitrogen before use.

**Solution Studies.** The characterization of the liquid clathrates was done by $^1$H NMR integration. For the toluene liquid clathrate, the 18-crown-6 resonance is observed at 3.07 ppm and that of $H_3O^+$ at 10.36 ppm. Those of the toluene are observed at 7.05 and 2.25 ppm. The resonance due to [Cl-H-Cl]$^-$ was not observed.

**Synthesis of [$H_3O$·18-crown-6][Cl-H-Cl].** A 1.32-g amount of 18-crown-6 (0.005 mol) was moistened with 0.09 mL of distilled water (0.005 mol), and ca. 30 mL of toluene was layered over the mixture, which was contained in a Schlenk tube. Anhydrous HCl(g) was bubbled

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0020-1669/90/1329-0467$02.50/0

**Table I.** Crystal Data and Summary of Data Collection

| compd | $[H_3O\cdot 18\text{-crown-}6][Cl-H-Cl]$ | $[K\cdot 18\text{-crown-}6][Cl-H-Cl]$ | $[Mg\cdot 18\text{-crown-}6][Cl-H-Cl]_2$ | $[H_3O\cdot 18\text{-crown-}6][Br-H-Br]$ |
|---|---|---|---|---|
| $M_r$ | 355.3 | 375.4 | 432.5 | 444.2 |
| space group | $P2_1/c$ | $P2_1/c$ | *Pbca* | $P2_1/c$ |
| cell const | | | | |
| *a*, Å | 10.475 (7) | 8.325 (2) | 18.310 (7) | 10.588 (1) |
| *b*, Å | 20.767 (9) | 14.094 (4) | 7.512 (6) | 21.060 (2) |
| *c*, Å | 8.583 (7) | 7.893 (4) | 29.085 (8) | 8.753 (1) |
| $\beta$, deg | 96.23 (3) | 98.56 (4) | | 95.25 (4) |
| *V*, Å$^3$ | 1856 (3) | 916 (2) | 4000 (4) | 1943 (1) |
| molecules/unit cell | 4 | 2 | 8 | 4 |
| *T*, °C | 22 | 22 | 22 | 22 |
| $D_c$, g cm$^{-3}$ | 1.28 | 1.37 | 1.44 | 1.52 |
| $\mu_c$, cm$^{-1}$ | 3.75 | 6.0 | 6.2 | 61.2 |
| radiation (graphite monochromated) | Mo K$\alpha$ | Mo K$\alpha$ | Mo K$\alpha$ | Cu K$\alpha$ |
| max cryst dimens, mm | 0.07 × 0.12 × 0.40 | 0.50 × 0.35 × 0.35 | 0.40 × 0.30 × 0.30 | 0.12 × 0.10 × 0.20 |
| scan width, deg | $0.80 + 0.20 \tan \theta$ | $0.80 + 0.20 \tan \theta$ | $0.65 + 0.20 \tan \theta$ | $0.80 + 0.14 \tan \theta$ |
| std reflcns | 200, 020, 002 | 200, 020, 002 | 200, 020, 002 | 400, 0120, 004 |
| decay of std | 1% | 21%[a] | 11%[a] | 2% |
| $2\theta$ range, deg | 2–48 | 2–48 | 2–44 | 2–112 |
| data collcn range | $h,k,\pm l$ | $h,k,\pm l$ | $h,k,l$ | $h,k,\pm l$ |
| no. of reflcns collcd | 1893 | 1629 | 2285 | 2499 |
| no. of obsd reflcns | 493 | 1194 | 1204 | 1697 |
| no. of params varied | 190 | 97 | 208 | 190 |
| GOF | 1.02 | 0.99 | 0.95 | 0.70 |
| *R* | 0.042 | 0.055 | 0.066 | 0.059 |
| $R_w$ | 0.047 | 0.050 | 0.066 | 0.065 |
| *w* | $[(\sigma_F)^2 + 0.000625F^2]^{-1}$ | $[(\sigma_F)^2 + 0.00009F^2]^{-1}$ | $[(\sigma_F)^2 + 0.00175F^2]^{-1}$ | $[(\sigma_F)^2]^{-1}$ |

[a] A correction for the crystal decomposition was applied.

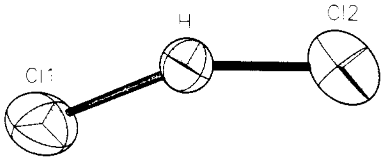

**Figure 1.** Structure of the $[Cl-H-Cl]^-$ anion in $[H_3O\cdot 18\text{-crown-}6][Cl-H-Cl]$.

through the solvent. Heat evolved, and two liquid layers appeared within 5 min. The passage of HCl(g) was continued until the lower liquid layer reached constant volume (ca. 30 min).

**Synthesis of $[K\cdot 18\text{-crown-}6][Cl-H-Cl]$.** Large colorless crystals of the potassium compound formed when 0.15 g of KCl (0.002 mol) was dissolved in the toluene liquid clathrate of $[H_3O\cdot 18\text{-crown-}6][Cl-H-Cl]$ (0.005 mol) at 80 °C and the mixture allowed to cool to room temperature. When collected, separated, and layered with toluene again, these crystals do not form a liquid clathrate.

**Synthesis of $[Mg\cdot 18\text{-crown-}6][Cl-H-Cl]_2$.** The preparation was the same as for the potassium salt, except that $MgCl_2$ dissolves only to the extent of 0.0005 mol in 0.005 mol of the $[H_3O\cdot 18\text{-crown-}6][Cl-H-Cl]$ liquid clathrate.

**Synthesis of $[H_3O\cdot 18\text{-crown-}6][Br-H-Br]$.** The preparation was the same as for the dichloride.

**X-ray Structure Determinations.** Single crystals of the compounds were sealed in thin-walled glass capillaries with a fraction of a drop of the liquid clathrate mother liquor from which they were crystallized. Details of usual procedures in our laboratory have been given previously.[6] A summary of data collection parameters and crystal data is presented in Table I. All structures were solved by using the direct methods program MULTAN,[7] and remaining non-hydrogen atoms were located by routine difference Fourier methods (calculated by using the SHELX suite of computer programs[8]). The hydrogen atom of the anion was located in a difference Fourier map for all of the $[Cl-H-Cl]^-$ salts, but in view of the difficulty of finding one electron between the two chlorine atoms, its parameters were not refined. In the hydrogen dibromide salt the hydrogen atom could not be located. In all cases the hydrogen atoms of the crown ether were placed at calculated positions ($d_{C-H}$ = 1.00 Å, H–C–H = 109.5°) and were not refined, rather being constrained to ride upon the appropriate carbon. Final fractional coordinates for the

**Table II.** Final Fractional Coordinates and $U_{eq}$ for $[H_3O\cdot 18\text{-crown-}6][Cl-H-Cl]$[a]

| atom | *x*/*a* | *y*/*b* | *z*/*c* | *U*(eqv),[b] Å$^2$ |
|---|---|---|---|---|
| Cl(1) | 0.3720 (5) | 0.1568 (2) | 0.4231 (6) | 0.097 (5) |
| Cl(2) | 0.5484 (5) | 0.0852 (3) | 0.2121 (7) | 0.106 (9) |
| O(1) | −0.219 (2) | 0.4659 (9) | 0.225 (2) | 0.108 (13) |
| O(2) | −0.329 (1) | 0.348 (1) | 0.260 (2) | 0.110 (24) |
| O(3) | −0.190 (2) | 0.2575 (7) | 0.434 (2) | 0.101 (6) |
| O(4) | 0.070 (1) | 0.2661 (7) | 0.468 (2) | 0.087 (17) |
| O(5) | 0.173 (1) | 0.386 (1) | 0.436 (2) | 0.096 (13) |
| O(6) | 0.045 (2) | 0.4775 (7) | 0.250 (2) | 0.095 (13) |
| O(7) | −0.0812 (9) | 0.3714 (5) | 0.371 (1) | 0.073 (14) |
| C(1) | −0.345 (3) | 0.450 (2) | 0.156 (3) | 0.143 (49) |
| C(2) | −0.403 (3) | 0.407 (2) | 0.251 (4) | 0.143 (73) |
| C(3) | 0.393 (3) | 0.300 (2) | 0.345 (4) | 0.162 (59) |
| C(4) | 0.313 (3) | 0.246 (1) | 0.347 (4) | 0.148 (21) |
| C(5) | 0.115 (3) | 0.200 (1) | 0.443 (3) | 0.121 (46) |
| C(6) | 0.006 (3) | 0.215 (1) | 0.537 (3) | 0.117 (52) |
| C(7) | 0.183 (2) | 0.286 (1) | 0.557 (2) | 0.095 (20) |
| C(8) | 0.254 (2) | 0.333 (1) | 0.469 (3) | 0.119 (37) |
| C(9) | 0.239 (2) | 0.434 (2) | 0.349 (4) | 0.132 (47) |
| C(10) | 0.166 (3) | 0.492 (1) | 0.339 (4) | 0.159 (5) |
| C(11) | −0.035 (3) | 0.530 (2) | 0.217 (5) | 0.183 (69) |
| C(12) | −0.158 (3) | 0.510 (2) | 0.145 (5) | 0.186 (18) |
| H | −0.4764 | 0.1241 | 0.3161 | 0.150 |

[a] Values in parentheses indicate the estimated standard deviation in the last figure. [b] $U(\text{eqv}) = {}^1/_3(U_{11} + U_{22} + U_{33})$.

**Table III.** Final Fractional Coordinates and $U_{eq}$ for $[K\cdot 18\text{-crown-}6][Cl-H-Cl]$[a]

| atom | *x*/*a* | *y*/*b* | *z*/*c* | *U*(eqv),[b] Å$^2$ |
|---|---|---|---|---|
| K | 1.0000 | 0.0000 | 0.0000 | 0.045 (3) |
| Cl | 0.8513 (1) | 0.00393 (5) | 0.3546 (1) | 0.065 (9) |
| O(1) | −0.2225 (2) | 0.1492 (1) | −0.0972 (2) | 0.047 (4) |
| O(2) | 0.0720 (2) | 0.1825 (1) | 0.1211 (2) | 0.049 (9) |
| O(3) | 0.3171 (2) | 0.0444 (1) | 0.1573 (2) | 0.049 (6) |
| C(1) | −0.1997 (3) | 0.2257 (2) | 0.0222 (3) | 0.054 (12) |
| C(2) | −0.0286 (3) | 0.2576 (2) | 0.0446 (3) | 0.052 (20) |
| C(3) | 0.2378 (3) | 0.2059 (2) | 0.1552 (3) | 0.055 (8) |
| C(4) | 0.3259 (3) | 0.1280 (2) | 0.2586 (3) | 0.054 (7) |
| C(5) | 0.3952 (3) | −0.0334 (2) | 0.2487 (4) | 0.059 (6) |
| C(6) | 0.3831 (3) | −0.1174 (2) | 0.1282 (4) | 0.062 (13) |
| H-Cl | 1.0000 | 0.0000 | 0.5000 | 0.070 |

[a] Values in parentheses indicate the estimated standard deviation in the last digit. [b] $U(\text{eqv}) = {}^1/_3(U_{11} + U_{22} + U_{33})$.

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**Table IV.** Final Fractional Coordinates and $U$(eqv) for [Mg·18-crown-6][Cl–H–Cl]$_2$[a]

| atom | $x/a$ | $y/b$ | $z/c$ | $U$(eqv),[b] Å$^2$ |
|---|---|---|---|---|
| Mg | 0.5007 (3) | –0.1556 (6) | 0.6191 (2) | 0.041 (14) |
| Cl(1) | 0.5353 (2) | 0.0340 (5) | 0.6842 (1) | 0.056 (13) |
| Cl(2) | 0.4720 (2) | –0.3425 (5) | 0.5534 (1) | 0.059 (24) |
| Cl(3) | 0.3169 (3) | –0.4527 (7) | 0.5042 (2) | 0.086 (3) |
| Cl(4) | 0.7081 (3) | –0.0436 (8) | 0.7139 (2) | 0.101 (14) |
| O(1) | 0.3961 (5) | –0.231 (1) | 0.6601 (4) | 0.051 (11) |
| O(2) | 0.5240 (6) | –0.413 (1) | 0.6562 (3) | 0.047 (13) |
| O(3) | 0.6214 (5) | –0.223 (1) | 0.6163 (4) | 0.053 (18) |
| O(4) | 0.5599 (6) | 0.032 (1) | 0.5724 (4) | 0.052 (22) |
| O(5) | 0.4192 (5) | 0.040 (1) | 0.5915 (3) | 0.049 (21) |
| O(6) | 0.2813 (6) | 0.042 (2) | 0.6573 (4) | 0.070 (11) |
| C(1) | 0.3986 (9) | –0.427 (2) | 0.6675 (7) | 0.067 (38) |
| C(2) | 0.4705 (9) | –0.469 (2) | 0.6893 (6) | 0.058 (21) |
| C(3) | 0.5976 (8) | –0.449 (2) | 0.6697 (6) | 0.052 (26) |
| C(4) | 0.6429 (9) | –0.406 (2) | 0.6283 (6) | 0.059 (28) |
| C(5) | 0.6636 (9) | –0.149 (2) | 0.5795 (6) | 0.062 (1) |
| C(6) | 0.6368 (9) | 0.041 (2) | 0.5773 (6) | 0.060 (32) |
| C(7) | 0.5251 (9) | 0.203 (2) | 0.5702 (6) | 0.058 (21) |
| C(8) | 0.4467 (9) | 0.160 (2) | 0.5572 (6) | 0.064 (20) |
| C(9) | 0.3435 (8) | 0.006 (2) | 0.5818 (6) | 0.059 (24) |
| C(10) | 0.2921 (9) | 0.100 (2) | 0.6123 (6) | 0.065 (16) |
| C(11) | 0.342 (1) | 0.043 (2) | 0.6865 (6) | 0.068 (31) |
| C(12) | 0.3661 (9) | –0.136 (2) | 0.6999 (6) | 0.076 (4) |
| HCl(1) | 0.6315 | –0.0208 | 0.7024 | 0.080 |
| HCl(2) | 0.3841 | –0.4348 | 0.5185 | 0.080 |

[a] Values in parentheses indicate the estimated standard deviation in the last digit. [b] $U(\text{eqv}) = {}^1/_3(U_{11} + U_{22} + U_{33})$.

**Table V.** Final Fractional Coordinates and $B$(eqv) for [H$_3$O·18-crown-6][Br–H–Br][a]

| | $x$ | $y$ | $z$ | $B$(eqv),[b] Å$^2$ |
|---|---|---|---|---|
| Br(1) | 0.3589 (1) | 0.15869 (6) | 0.4365 (2) | 7.78 (3) |
| Br(2) | 0.5504 (1) | 0.08192 (7) | 0.2096 (2) | 8.35 (4) |
| O(1) | 0.1624 (6) | 0.3896 (4) | 0.4358 (9) | 7.6 (2) |
| O(2) | 0.0641 (6) | 0.2694 (3) | 0.4788 (8) | 7.0 (2) |
| O(3) | –0.1948 (7) | 0.2568 (4) | 0.437 (1) | 8.2 (2) |
| O(4) | –0.3297 (7) | 0.3449 (5) | 0.267 (1) | 9.2 (2) |
| O(5) | –0.2242 (8) | 0.4606 (4) | 0.222 (1) | 9.4 (2) |
| O(6) | 0.0318 (8) | 0.4752 (4) | 0.243 (1) | 9.0 (2) |
| O(7) | –0.0885 (6) | 0.3714 (3) | 0.3763 (9) | 6.8 (2) |
| C(1) | 0.2422 (9) | 0.3359 (7) | 0.477 (1) | 8.5 (3) |
| C(2) | 0.173 (1) | 0.2926 (6) | 0.570 (1) | 8.5 (3) |
| C(3) | 0.002 (1) | 0.2189 (5) | 0.550 (1) | 8.8 (4) |
| C(4) | –0.115 (1) | 0.2035 (6) | 0.452 (2) | 9.5 (4) |
| C(5) | –0.311 (1) | 0.2403 (7) | 0.353 (2) | 11.8 (5) |
| C(6) | –0.390 (1) | 0.2984 (9) | 0.344 (2) | 12.0 (5) |
| C(7) | –0.402 (1) | 0.4045 (8) | 0.253 (2) | 11.7 (4) |
| C(8) | –0.347 (1) | 0.4465 (8) | 0.148 (2) | 10.9 (4) |
| C(9) | –0.172 (2) | 0.5035 (8) | 0.131 (2) | 14.7 (6) |
| C(10) | –0.056 (2) | 0.5264 (6) | 0.212 (2) | 13.1 (5) |
| C(11) | 0.146 (1) | 0.4918 (7) | 0.329 (2) | 12.0 (5) |
| C(12) | 0.227 (1) | 0.4335 (7) | 0.350 (2) | 10.2 (4) |

[a] Values in parentheses indicate the estimated standard deviation in the last digit. [b] $B(\text{eqv}) = {}^1/_3(U_{11} + U_{22} + U_{33})(8\pi^2)$.

[H$_3$O·18-crown-6][Cl–H–Cl], [K·18-crown-6][Cl–H–Cl], [Mg·18-crown-6][Cl–H–Cl]$_2$, and [H$_3$O·18-crown-6][Br–H–Br] salts are given in Tables II–V.

## Results and Discussion

The reaction of HCl(g), H$_2$O, and 18-crown-6 in toluene according to eq 2 yields a liquid clathrate of composition [H$_3$O·18-crown-6][Cl–H–Cl]·3.6tol. The analogous benzene liquid clathrate has 4.8 benzene molecules per cation/anion pair. In the structure of the parent salt there are not remarkably short cation···anion separations (the closest contact is between Cl(1) and C(12), 3.61 Å). The anion, shown in Figure 1 has no crystallographically imposed symmetry. The Cl···Cl separation is 3.11 (1) Å, and the hydrogen atom is located 1.47 and 1.65 Å from the two chlorine atoms. The Cl–H–Cl angle is 168°.

For [K·18-crown-6][Cl–H–Cl], the anion and indeed the bridging hydrogen atom reside on a crystallographic center of inversion. The hydrogen atom is therefore centered between the two chlorine atoms with equal H···Cl distances of 1.56 Å. The Cl···Cl separation is 3.117(1) Å.

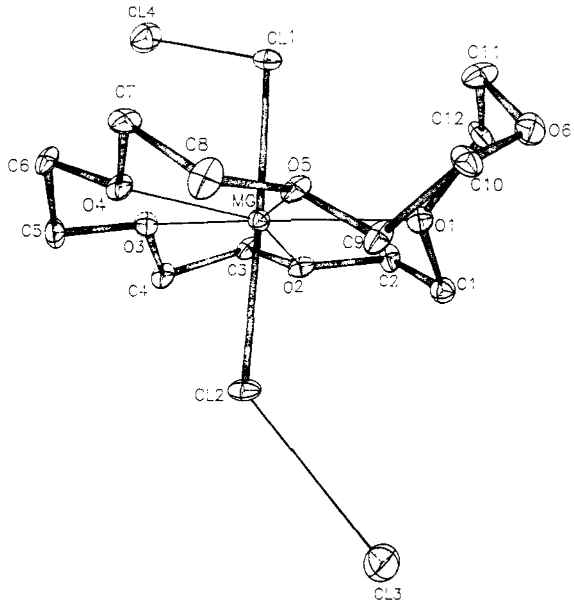

**Figure 2.** Structure of the [Mg·18-crown-6]$^{2+}$ ion.

In [Mg·18-crown-6][Cl–H–Cl]$_2$, the ions have no crystallographic symmetry. The hydrogen atoms in the two independent anions lie on the line of the chlorine atoms and nearer the nonmetal-bound one. The Cl···Cl separations are 3.286 (1) and 3.331 (1) Å.

Table VI presents the Cl···Cl distances for the hydrogen dichloride anion with a range of cations.[9-12] The K$^+$ and H$_3$O$^+$ derivatives are at the short end of the range, and the Mg$^{2+}$ compound is at the long end. A central question here is whether or not the dichloride ion is symmetrical.[13] This also relates to the Cl···Cl distance. Although the hydrogen atoms in the title structures have not been located with great accuracy, they still afford the basis for comparisons.

First, the Cl···Cl distances may be understood in terms of the cation/anion interactions. The strong bond between the magnesium and chlorine atoms (mean 2.441 (7) Å)[14] (Figure 2) apparently weakens the hydrogen bonding and thus lengthens the Cl···Cl separation. With the potassium salt, the K···Cl distance of 3.225 (1) Å is a normal electrostatic bond (cf. the sum of the van der Waals radii, 3.14 Å[13]) and the Cl···Cl separation is lowered to 3.117 (1) Å. In the oxonium compound there are similarly no strong directional contacts between the cation and the anion.

Second, the hydrogen atoms in the magnesium structure are closer to the chlorine atoms that are not bonded to the magnesium atom. This is expected, and it is a likely consequence of the Mg–Cl bond. On the other hand, with the potassium compound the two chlorine atoms are equally involved in electrostatic interactions and the hydrogen atom is centered. For the oxonium compound the two chlorine atoms are not in very different electrostatic

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(14) The Mg–Cl bond lengths, 2.428 (6) and 2.454 (6) Å, agree well with the 2.429 (2) Å value found in [Mg·18-crown-6]Cl$_2$[27] but are shorter than (a) the 2.50 Å found for Mg–Cl–Mg bridges (Sobota, P.; Utko, J.; Lis, T. *J. Chem. Soc., Dalton Trans.* **1984**, *2077*) or (b) the 2.5 Å estimate for six-coordinate magnesium (Toney, J.; Stucky, G. D. *J. Organomet. Chem.* **1971**, *28*, 5).

(15) The estimate for K···Cl is based on the Li–Cl bond length of 2.40 Å (Durant, F.; Gobillon, Y.; Piret, P.; van Meerssche, M. *Bull. Soc. Chim. Belg.* **1966**, *75*, 52) and the sum of ionic radii is 3.1 Å.

**Table VI.** Comparison of Structural Parameters for $[Cl-H-Cl]^-$

| Cl⋯Cl, Å | Cl-H, Å | H-Cl, Å | Cl-H-Cl, deg | compd | ref |
|---|---|---|---|---|---|
| 3.11 (1) | 1.47 | 1.65 | 168 | $[H_3O{\cdot}18\text{-crown-}6][Cl-H-Cl]$ | 5 |
| 3.117 (1) | 1.56 | 1.56 | 180 | $[K{\cdot}18\text{-crown-}6][Cl-H-Cl]$ | *a* |
| 3.121 (2) | 1.54 | 1.74 | 144 | $[(4\text{-}MeOC_6H_4)PCl_3][Cl-H-Cl]$ | 7 |
| 3.14 (2) | | | | $CsCl{\cdot}{}^1/_3([H_3O][Cl-H-Cl])$ | 8 |
| 3.189 (1) | 1.39 | 1.81 | 170 | $[(4\text{-}EtOC_6H_4)PCl_3][Cl-H-Cl]$ | 7 |
| 3.210 (3) | 1.36 | 1.86 | 172 | $[(4\text{-}MeOC_6H_4)(Me)PCl_2][Cl-H-Cl]$ | 7, 9 |
| 3.22 | 1.40 | 1.82 | 180 | $[NMe_4][Cl-H-Cl]$ | 10 |
| 3.288 (2) | 1.20 | 2.18 | 151 | $[(4\text{-}MeOC_6H_4)PCl_3][Cl-H-Cl]$ | 7 |
| 3.286 (1) | 1.30 | 2.03 | 161 | $[Mg{\cdot}18\text{-crown-}6][Cl-H-Cl]_2$ | *a* |
| 3.331 (1) | 1.45 | 1.88 | 173 | | |

[a] This study.

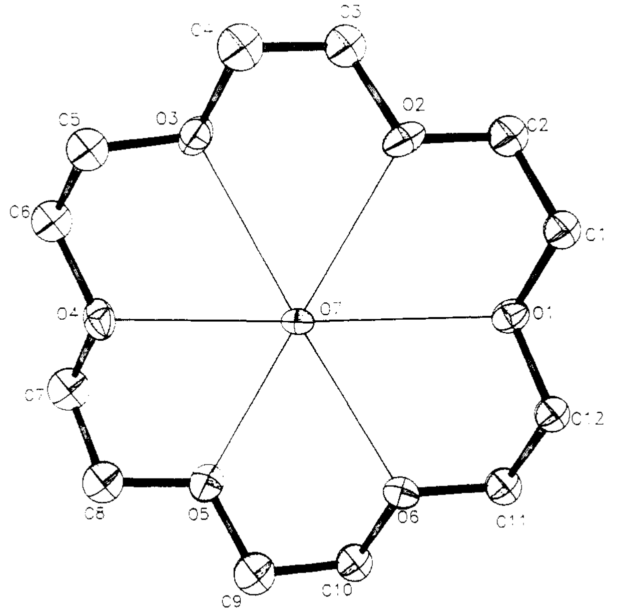

**Figure 3.** Structure of the $[H_3O{\cdot}18\text{-crown-}6]^+$ ion in $[H_3O{\cdot}18\text{-crown-}6][Cl-H-Cl]$. The hydrogen atoms of the cation are disordered and could not be located. The hydrogen-bonding scheme is indicated by thin O⋯O lines.

situations and the hydrogen atom is therefore effectively centered, within the accuracy of the experiment. In summary, we propose that the centered hydrogen atom should be most prevalent with the short Cl⋯Cl separations, which in turn arise from the lack of strong directional bonds to the chlorine atoms.

In the $[Br-H-Br]^-$ anion, the Br⋯Br separation, 3.377 (1) Å, compares favorably with the only other such determination, 3.35 Å in $CsCl{\cdot}{}^1/_3([H_3O][Br-H-Br])$.[10]

With regard to the $[H_3O{\cdot}18\text{-crown-}6]^+$ cation, the oxonium hydrogen atoms could not be located for either the $[Cl-H-Cl]^-$ or $[Br-H-Br]^-$ salts, presumably because of disorder, as indicated in Figure 3. The O(oxonium)⋯O(crown) distances for the $[Cl-H-Cl]^-$ salt (with those for the $[Br-H-Br]^-$ salt given in parentheses) range from 2.70 to 2.85 Å (2.69 to 2.84 Å) and are well within the range indicative of hydrogen bonding.[16] The oxonium oxygen atom lies 0.29 Å (0.29 Å) out of the mean plane of the crown ether oxygen atoms, which are coplanar to within 0.20 Å (0.23 Å). There have been two previous structural reports of the oxonium ion bonded to 18-crown-6.[17,18] In one the coordination was interpreted as planar,[17] while in the other the oxonium was viewed as tetrahedral.[18] For the planar $H_3O^+$ the oxygen atom was 0.10 Å out of the plane of the crown, and for the tetrahedral $H_3O^+$ the value was 0.61 Å. Thus, the hydronium ions discussed here lie between the cited extremes.[19]

It is worthwhile to note that while numerous reports of the oxonium ion bonded to a macrocycle have appeared since 1972,[17,19,20-25] the title compounds are the first examples of the oxonium ion complexed in aromatic solvents.

The coordination of the magnesium ion in the $[Mg{\cdot}18\text{-crown-}6]^{2+}$ ion is worthy of discussion. The magnesium atom is coordinated (Figure 2) to only five oxygen atoms of the crown at distances of 2.24 (1)–2.33 (1) Å,[26] the sixth oxygen atom at 4.424 (4) Å being well out of range. This is further illustrated by the best planes calculations, which show the magnesium atom to be within 0.01 Å of the plane of the five bonded oxygen atoms (which are coplanar to within 0.20 Å). The sixth oxygen atom lies 0.84 Å out of this plane. The remainder of the coordination sphere of the magnesium atom is occupied by two chlorine atoms of the anions at 2.428 (6) and 2.454 (6) Å. Recent examples of the use of macrocycles to stabilize six-[27] and eight-coordinate magnesium[28] have appeared, but to our knowledge this is the third example of a seven-coordinate magnesium atom.[25,29]

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**Supplementary Material Available:** For the four structures, tables of hydrogen coordinates, bond lengths and angles, and isotropic thermal parameters and figures showing stereoviews of the cell packing (14 pages); listings of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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