Database Studies of Halide Ion Pairs with Bridging Water and NH_2 Amino Molecules

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Studies using the Cambridge Structural Database have shown that hydrogen-bond linearity is a major factor determining the structure of halide ion pairs bridged by water and NH_2-containing molecules and that the halide–halide distances in these ion pairs are geometrical consequences of this fact.

There has been much recent interest in ionic solvation and it has been reported that ions of like charge such as Cl^- and Cl^- may approach one another to within short distances to form hydrogen-bonded ion pairs with bridging water molecules.[1,2] These species are referred to as contact ion pairs with bridging water molecules (CIPBWs). This phenomenon has been studied theoretically[1–3] but experimental verification in solution is difficult. The possibility of studying CIPBWs in crystals with the Cambridge Structural Database (CSD)[4] appears to be immediately obvious. However, two sets of workers who have recently studied this problem have commented upon the failure of the CSD searches to detect CIPBWs properly or exhaustively.[5,6] These comments have prompted the present study which examines the phenomenon of water-bridged chloride ion pairs in crystals and also extends it to other halide ions and other hydrogen-bonded bridging groups.

In this paper we have investigated the geometrical properties of halide ion pairs bridged by AH_2 (A = O or N) with each of the hydrogen atoms of AH_2 being hydrogen bonded to each particular halide ion. A total of 4293 halide-containing structures are available in the CSD (Version 4, 1990 update with 82 129 entries). The distribution of various halide ions, with and without water of crystallisation, is given in Table 1.

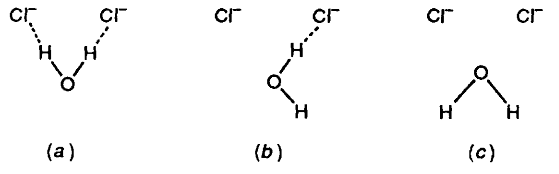
Table 1 General distribution of various halides with and without water of crystallisation obtained as hits from the QUEST search[a]

	Water of crystallisation		
Halide	Absent	Present	Ratio[b]
F	25	16	1.56
Cl	1404	860	1.63
Br	760	319	2.38
I	731	163	4.48

[a] Fifteen mixed-halide structures were excluded and so the total number of retrieved structures is 4293. [b] Ratio = (number of water-absent structures)/(number of water-present structures).

Experimental

Database Searches.—All geometrical calculations were performed with GSTAT 90.[4] The following precautions were taken to obtain reliable and accurate results. As GSTAT cannot distinguish between a halide ion and a bonded halogen atom during calculations, covalently bonded halogen atom-containing-structures were avoided, while retrieving a particular halide ion-containing-structure. Even so, many structures are available in each category, thus ensuring reliable conclusions. For all calculations, error-containing, polymeric or disordered structures were eliminated. Duplicate structures and those with *R* factors greater than 0.075 were also not considered. The average values of various parameters are cited with the corresponding standard deviations of the mean. Typical QUEST and GSTAT questions are given in Table 2.



In GSTAT calculations performed previously[5,6] both groups of workers fixed the $Cl^- \cdots Cl^-$ and $Cl^- \cdots O$ distances as geometrical criteria for a CIPBW. However, by fixing the $Cl^- \cdots O$ distance in the 3.2 Å region (required for a hydrogen bond between water and Cl^-), three major possibilities were found. Though the $Cl^- \cdots O$ distance is within the desired range in all these cases, only (*a*) is relevant here. So we restricted the $X^- \cdots X^-$ distance (X = F, Cl, Br or I) to the range 3.0–6.0 Å and additionally both the $X^- \cdots H$ distances to be within the range for hydrogen-bond formation (1.5–3.0 Å). This procedure ensures that only type (*a*) fragments are obtained. This automatically restricts the $X^- \cdots O$ to the desired range (2.0–4.0 Å). The problem of H atom positions being determined less accurately by X-ray diffraction techniques was overcome by using the HNORM option available in GSTAT. This moves the H atom position along the A–H vector to a distance which is similar to the A–H neutron bond length (0.983 Å for water and 1.009 Å for N–H). Usually then the $X^- \cdots H$ distance appeared in the range 1.5–3.0 Å.

Gao *et al.*[5] stated that they restricted their studies to 'the primary unit cell', However it should be noted that in the CSD set of programs one can restrict calculations only to a single molecule and not to a single unit cell. Kleinman *et al.*[6] stated that CSD entries are generated using a minimum number of symmetry operators and so 'CIPBWs between cells may be missed' in GSTAT calculations. However, it must be emphasised that GSTAT takes into account all the fragments in the crystal which satisfy the geometrical conditions specified by the user, without reference to whether a unit-cell boundary is crossed or not. The comments of the previous workers must therefore be considered with some reservation, though in all fairness neither group mentioned the version of the CSD employed. In our hands the 1990 version generated a much larger number of genuine CIPBWs than were obtained previously. Further we extended the study to other halide ions and the results correlate well with the theoretical studies and so reiterate the suitability of the CSD for this kind of study.

Table 2 Sample QUEST and GSTAT questions used in the present studies

```
QUEST
Save 3
SSStop 3000
T1 *CONN
AT1 CL 99 99 49
END
T2 *RESI 'H2 + O1'
T3 *CONN
AT1 AA 1
AT2 CL 1
BO 1 2
END
QUEST (T1).AND.(T2).AND.(.NOT.T3)

GSTAT
BRI
NOD
HNORM
NDIS
NPOL
NERR
RFAC 0.002, 0.075
CALC INTER FROM CL 3.0 TO CL 3.0 EXT
FRAG CHLORIDE
AT1 CL 0
AT2 H 1
AT3 O 2
AT4 H 1
AT5 CL 0
BO 2 3
BO 3 4
BO 1 5
TEST DIST 1 5 3.0 6.0
TEST DIST 1 2 1.5 3.0
TEST DIST 4 5 1.5 3.0
END
```

Table 3 Average interhalide distances (Å) in the presence and absence of water of crystallisation (numbers in parentheses indicate numbers of hits)

	Water of crystallisation	
Halide	Absent	Present
F	4.82 ± 0.13 (39)	4.90 ± 0.39 (4)
Cl	5.10 ± 0.02 (684)	5.07 ± 0.02 (686)
Br	5.20 ± 0.04 (232)	5.32 ± 0.03 (240)
I	5.32 ± 0.04 (181)	5.28 ± 0.04 (109)

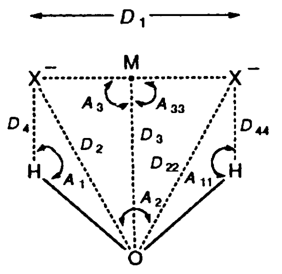


Fig. 1 Definition of lengths and angles in the ClPBW fragment; M is the midpoint of the interhalide vector

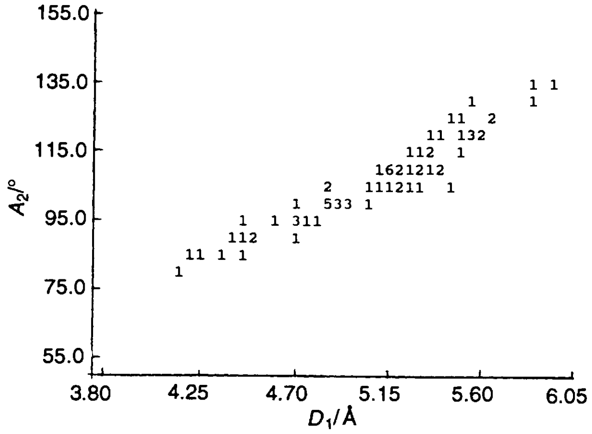


Fig. 2 Scatterplot of the interhalide Cl$^-$ ··· Cl$^-$ distance, D_1, *versus* angle A_2

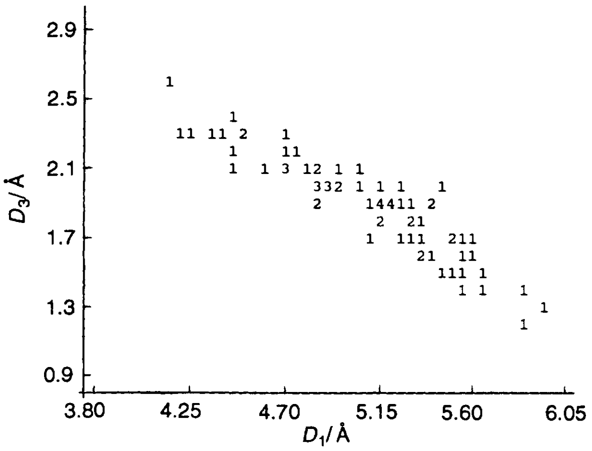


Fig. 3 Scatterplot of the interhalide Cl$^-$ ··· Cl$^-$ distance, D_1, *versus* distance D_3

Results and Discussion

A preliminary survey of X$^-$ ··· X$^-$ distances within the range 3.0–6.0 Å was carried out. The results (Table 3) indicate that the interhalide ion separation is largely insensitive to the presence or absence of water of crystallisation in the structure. This may hint that water specifically has no role in bringing the two halide ions to these short distances and may confirm the statement made in an earlier theoretical study[3] that 'the stable minimum near contact is stabilised, *in part* (our italics) due to the presence of several bridging water molecules'. Fig. 1 shows a sketch of the fragment used for the calculations. In all cases, the distance D_{22} is defined to be shorter than D_2.

Another interesting feature encompassing all aspects of this study is that one should expect symmetrical hydrogen bonding on either arm of the H–A–H fragment of these species because the average environment around the two halide ions should be comparable. In other words, in Fig. 1, D_2 should be equal to D_{22} and D_4 to D_{44}. However it was found that this is not the case for a majority of the compounds (except for F$^-$ ion pairs). The results are presented according to the halide ion and the number of water or other molecules present.

Chlorides with Water.—For water-bridged (one water molecule) structures there are 76 hits from 682 structures and the results are given in Table 4. There is a continuous distribution of D_1 values throughout the range 4.17–5.96 Å whereas D_2 is confined to the range 3.06–3.39 Å. As expected, the correlation coefficient for the scatterplot of D_1 *versus* D_2 is very poor (0.14). A similar pattern was observed when D_1 was correlated with the other parameters associated with the hydrogen bonding, *i.e.* D_{22}, D_4, D_{44}, A_1 and A_{11}. All this shows that the water molecule is linearly hydrogen bonded to the chloride ion pair, but that the interchloride distance, D_1, does not correlate satisfactorily with the hydrogen-bonding parameters. Interestingly, Figs. 2 and 3

Table 4 Mean values of various geometrical parameters for halide ion pairs

				Distance/Å						Angle/°		
Halide[a]	No. of entries	AH_2	No. of hits	D_1	D_2	D_{22}	D_3	D_4	D_{44}	A_1	A_{11}	A_2
Cl(+)	682	H_2O	76	5.08(5)	3.22(1)	3.16(1)	1.90(3)	2.31(1)	2.21(1)	168(8)	156(2)	106(1)
		H_2O[b]	1	5.29	3.32	3.20	1.91	2.38	2.30	177	177	108
		NH_2	62	4.92(7)	3.29(1)	3.21(1)	2.08(5)	2.45(3)	2.25(2)	163(1)	142(2)	99(2)
		NH_2[b]	1	5.88	3.35	3.17	1.41	2.68	2.15	174	125	129
Cl(−)	1093	NH_2	167	5.03(4)	3.26(1)	3.18(1)	1.97(3)	2.39(2)	2.21(1)	165(1)	149(1)	104(1)
		NH_2[c]	10	5.13(20)	3.22(2)	3.17(2)	1.87(10)	2.27(6)	2.16(2)	168(2)	157(6)	108(4)
		ND_2	2	4.53(15)	3.21(8)	3.10(2)	2.19(16)	2.44(32)	2.08(0)	164(1)	135(28)	92(6)
Br(+)	303	H_2O	21	5.36(8)	3.36(2)	3.30(2)	1.96(5)	2.44(3)	2.36(2)	167(2)	156(3)	108(2)
		NH_2	12	5.51(9)	3.53(3)	3.44(2)	2.12(8)	2.67(4)	2.49(3)	159(2)	144(2)	105(3)
Br(−)	674	NH_2	26	5.28(8)	3.42(2)	3.35(2)	2.10(4)	2.51(3)	2.40(2)	165(2)	149(3)	103(2)
I(+)	151	H_2O	1	5.24	3.56	3.49	2.36	2.59	2.52	167	166	96
		NH_2	2	5.42(30)	3.82(2)	3.62(8)	2.54(22)	2.86(1)	2.72(11)	160(7)	149(4)	94(8)
I(−)	643	NH_2	7	5.47(17)	3.64(4)	3.60(3)	2.35(11)	2.68(5)	2.61(4)	170(2)	158(3)	99(4)
		NH_2[c]	2	5.08(2)	3.52(0)	3.52(0)	2.44(1)	2.52(2)	2.53(3)	165(8)	165(8)	92(1)

[a] (+) Represents the presence of water of crystallisation, (−) its absence. [b] Neutron diffraction study. [c] Ligated water molecules.

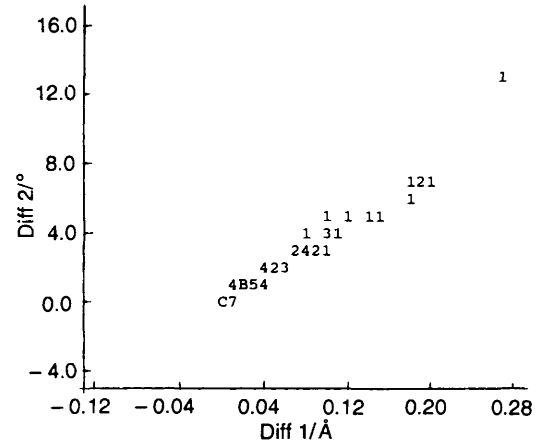


Fig. 4 Scatterplot of the difference, Diff 1, between distances D_2 and D_{22} *versus* the difference, Diff 2, between angles A_3 and A_{33} for $Cl^- \cdots Cl^-$ ion pairs. $B = 11$ and $C = 12$

show that D_1 is well correlated, with the $Cl^- \cdots O \cdots Cl^-$ angle, A_2 (0.97), and with the distance D_3 (−0.93). These purely geometrical correlations clearly indicate that while the $Cl^- \cdots O$ distance, D_2, is critical and is maintained for optimum linear hydrogen bonding, A_2 and D_3 vary according to the resulting D_1 value. In other words, both the Cl–O sides of the triangle Cl–O–Cl are fixed (by hydrogen bonding) and so the other parameters adjust themselves according to the third side (D_1). Distance D_3 has an excellent correlation with A_2 (0.99), further confirming this assumption. The distances D_2 and D_{22} are in the range 3.01–3.39 Å, which is well within the range for linear hydrogen bonding. Scatterplots were generated of D_1 (or D_3) *versus* the angle between the planes of $Cl^- \cdots O \cdots Cl^-$ and HOH to see whether the $Cl^- \cdots Cl^-$ separation was determining the arrangement of H_2O or *vice versa*. However, they were featureless.

The dissimilarity in both the $Cl^- \cdots O$ distances was examined by correlating the difference between these two distances, Diff 1 = $D_2 - D_{22}$, with that of other geometrical parameters of the fragment. Fig. 4 shows that the difference between the greater and lesser of the angles, $Cl^- \cdots M \cdots O$, Diff 2, correlates excellently with Diff 1 (0.99). This indicates that the vector O–M is not the perpendicular bisector of the interhalide $X^- \cdots X^-$ vector, but slightly tilted towards one of the chloride ions. Though this shift is small, the effect is significant (≈0.03 Å per degree).

The mean values obtained here for $Cl^- \cdots O$ (3.22, 3.16 Å) and $Cl^- \cdots H$ (2.31, 2.21 Å) are in good agreement with those predicted in the earlier theoretical studies (3.21 and 2.25 Å).[7] Additionally the position of the second peak in the ion–hydrogen radial distribution function corresponding to the non-bonded hydrogen atoms of the first-shell water molecules as obtained by Jorgensen and co-workers[7] also correlates well with the $Cl^- \cdots H$ (non-bonded) distance of the fragment [3.57(2) Å].

For two water molecules there are three hits and here too the differences in non-bonded distances are present and these differ for each water molecule of the fragment. Both waters are not in plane [average deviation 56(9)°] and the two oxygens are separated by a distance of 3.72(10) Å and the chlorides by 4.95(21) Å. These figures are not mentioned in Table 4.

Chlorides with NH_2 *Amino Molecules.*—There are 62 hits with NH_2-bridged chloride pairs and the average $Cl^- \cdots Cl^-$ distance is 4.92(7) Å. All other features are common to those for water-bridged fragments. There is one hit each with neutron-diffraction studies for H_2O and NH_2 bridges. There are 167 hits with NH_2 bridging in structures not containing water of crystallisation. The average D_2 and D_{22} values indicate relatively stronger hydrogen bonds here when compared to the NH_2-bridged pairs in structures which contain additional water.

Bromides and Iodides.—With H_2O there are 21 hits for Br^- and the average $Br^- \cdots Br^-$ distance is 5.36 Å. Here too the average $Br^- \cdots O$ distances are 3.36 and 3.30 Å and $Br^- \cdots H$ distances are 2.44 and 2.36 Å. The hydrogen bond angles are 166.7 and 156.2°, thus indicating that, for bromide ion pairs too, water forms essentially linear hydrogen bonds. All other correlations are similar to those observed for chlorides. There is only one hit for an I^- ion pair with water bridging. Similarly there is one I^- ion pair with two bridging water molecules also present and here the hydrogen bonds are perfectly linear (179.9°). The details of the ion pairs with bridging NH_2 are given in Table 4.

Fluorides.—There are less F^--containing structures in the CSD in comparison with other halide structures (Table 1). Correspondingly, there is only one F^- ion pair with two bridging water molecules, with $F^- \cdots F^-$ being 4.06 Å. It is interesting that the hydrogen bonds are perfectly symmetrical with the $O \cdots O$ vector perpendicular to the $F^- \cdots F^-$ vector. The great strength of the $F^- \cdots H–O$ hydrogen bond is the probable reason for this observation.

Conclusion

These database studies confirm the earlier theoretical predictions of Buckner and Jorgensen[2] that 'a structure in which a water molecule uses both hydrogens to linearly hydrogen bond to two chloride ions would then require an interionic distance of 5.0–5.10 Å', that is the interchloride distance is a geometrical consequence of hydrogen bonding, and of Dang and Pettitt,[3] who stated that the 'potentials of mean force of like negative ion pairs at extreme dilution display a stable minimum near contact and this minimum is stabilised in part due to the presence of several bridging water molecules'.

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