

Metal-bound chlorine often accepts hydrogen bonds

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Analysis of 6624 crystallographically characterised hydrogen bonds containing M–Cl, C–Cl or Cl[−] and either HO or HN groups show that M–Cl moieties are good, anisotropic hydrogen-bond acceptors forming hydrogen bonds similar in length to those of the chloride anion, while C–Cl moieties are very poor hydrogen-bond acceptors.

In a recent article,¹ Dunitz and Taylor showed that the hydrogen bonding capability of the C–F moiety is very poor on the basis of a crystal structure database study and quantum mechanical calculations. The implication of that work is that hydrogen bonding D–H...F–C (D = O, N, *etc.*) interactions are too weak to be of great significance in molecular recognition processes in, for example, biological chemistry or crystal engineering. Here, we show that although C–Cl moieties and C–F have rather similar hydrogen-bonding characteristics, M–Cl moieties (M = transition metal) are much better hydrogen-bond acceptors. The ability of metal halide species to act as hydrogen-bond acceptors has been noted anecdotally by us and others on the basis of one or more crystal structures.² Braga, Desiraju and Grepioni and coworkers³ have shown that ligands in organometallic complexes can be involved in hydrogen bonding. In the systems they have studied the ligands are either rather weak acceptors (*e.g.* carbon monoxide) or behave essentially as their organic analogues do. In the inorganic species studied here (those with terminal M–Cl bonds) the effects of the metal on the

hydrogen-bonding ability of the ligand are much more dramatic, in a way not anticipated in recent authoritative texts on hydrogen bonding.⁴ Indeed Jeffery states 'while halide ions are strong hydrogen-bond acceptors, there is no evidence from crystal structures supporting hydrogen bonds to halogens.'^{4a} Here we show that (as Dance has speculated)⁵ in contrast, metal bound chlorine is a good hydrogen bond acceptor.

To assess the hydrogen-bonding capabilities of the M–Cl unit, the Cambridge Structural Database⁶ was used to search for structures containing O–H or N–H fragments as well as M–Cl, Cl[−] or C–Cl.† Our objective was to compare the geometry of D–H...Cl–M interaction in these crystal structures as well as to assess the relative probability of such contacts being formed to chlorine in these three different forms. The intermolecular contacts were categorised as 'short' (≤2.52 Å), intermediate

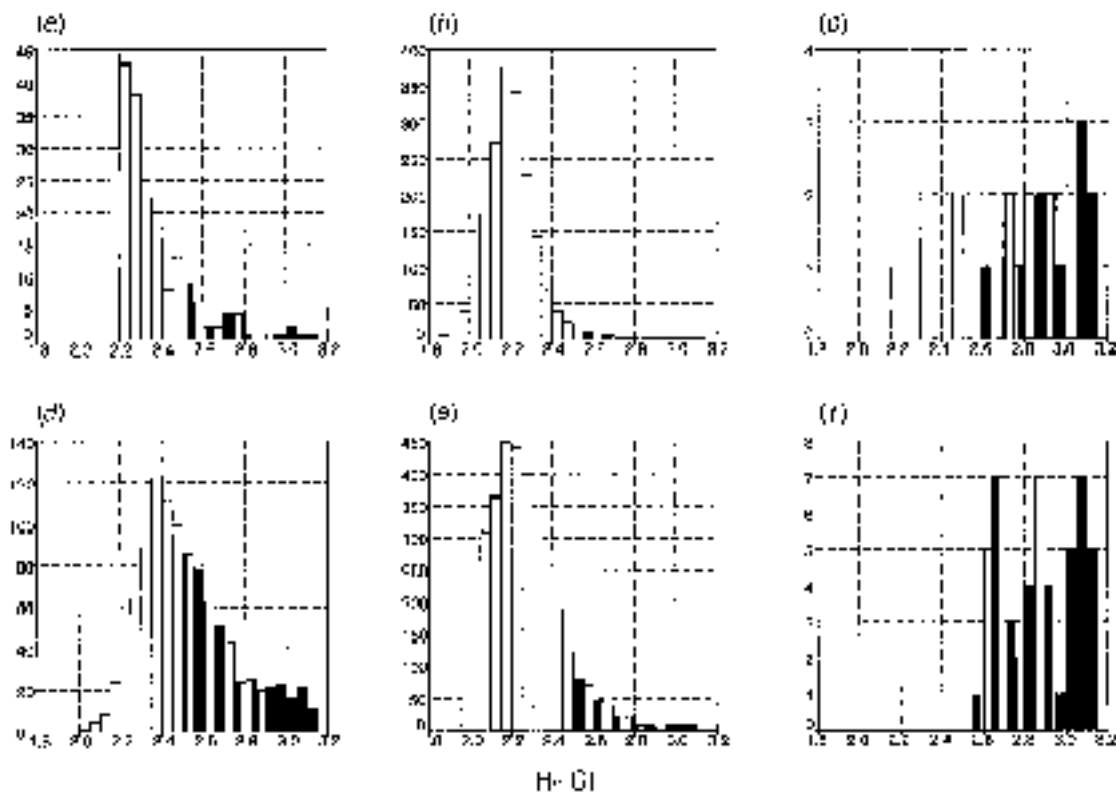
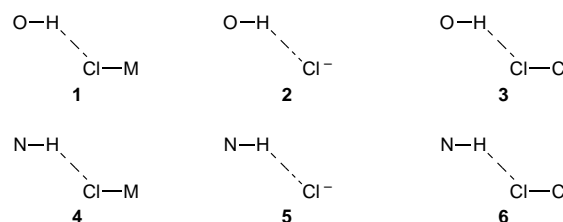


Fig. 1 Histograms of H...Cl distances for (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6. Short distances in light grey, intermediate in grey, long in black.

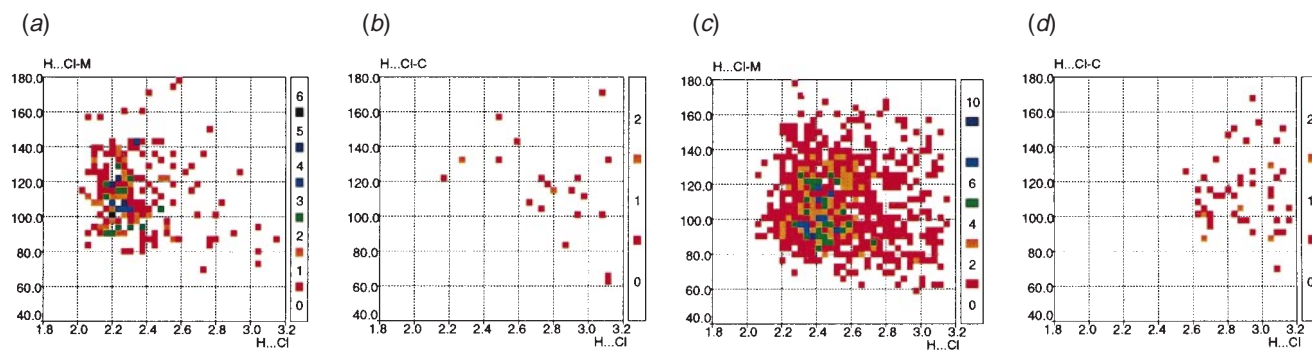


Fig. 2 Scattergrams of M–Cl...H or C–Cl...H angles vs. H...Cl distances in systems (a) **1**, (b) **3**, (c) **4**, (d) **6**. The number of cases in a given pixel are colour coded.

Table 1 Percentage of hydrogen-bond contacts (H...Cl \leq 3.15 Å) which were classified as short (H...Cl \leq 2.52 Å)

Interaction	D = O	D = N
D–H...Cl–M	86.5 1	57.4 4
D–H...Cl [–]	97.2 2	90.8 5
D–H...Cl–C	22.7 ^a 3	0.0 6

^a Represents five observations (out of a total of 22 O–H...Cl–C contacts \leq 3.15 Å).

(2.52–2.95 Å) and long 2.95–3.15 Å (*cf.* sum of van der Waals radii for H and Cl = 1.2 + 1.75 = 2.95 Å).⁷

The range of H...Cl distances for the cases shown in Scheme 1 are illustrated in Fig. 1. It is clear that Cl[–] forms many ‘short’ Cl...H interactions, as does the M–Cl group, whereas C–Cl moieties form almost no ‘short’ Cl...H interactions. The correlation of D–H...Cl angles with H...Cl distance (see Supplementary material[§]) is comparable to that typically observed for the corresponding parameters in both strong and weak hydrogen bonds, and shows a predominance of D–H...Cl angles close to 180° at short H...Cl separations.⁸

Fig. 2 shows the spread of M–Cl...H and C–Cl...H angles with respect to H...Cl distance.¶ It is clear from examination of Fig. 2(a) that there is a clustering of structures for M–Cl acceptors, particularly in the short distance range, at angles of *ca.* 100–110°, suggesting some directional preference in these interactions. The C–Cl acceptors [Fig. 2(b),(d)] appear to favour a similar range of angular approaches, through there are fewer data, and almost no stronger, shorter Cl...H interactions.

The percentage of interactions formed that fall in the various categories (in particular the ‘short’ group, Table 1) may be taken as an indicator of the strength of the interactions of types **1–6**. These percentages confirm the expectation that in general O–H is a stronger donor than N–H, and more importantly that the sequence of acceptor strengths is Cl[–] > M–Cl \gg C–Cl.

The clear implication of these observations is that M–Cl containing complexes have the potential to interact with hydrogen-bond donors in both a strong (*i.e.* short) and anisotropic fashion. In the first respect they resemble the chloride ion and in the second organochlorine species. The shortness of D–H...Cl–M bonds presumably derives at least in part from the large negative charge on the chloride in these partially ionic M–Cl bonds. The poor hydrogen-bond acceptor qualities of C–Cl, C–F, *etc.* may in turn be associated with much lower charge accumulation at the halogen atom in these species.¹

Rheingold, Crabtree and their coworkers showed that the structure of [HNC₅H₃Ph₂-2,6][AuCl₄] was consistent with greater basicity of chlorine p than sp lone pairs,^{2c} since there appeared to be preference for their involvement in the N–H...Cl–M bonds. In this work we have shown that this is not an isolated occurrence and that this phenomenon may be much more general than has hitherto been thought.

These observations may be extended to metal complexes of the other halides, which although less numerous show similar patterns of behaviour in structures in the CSD. We are exploring the application of these observations to the design and synthesis of crystal structures of metal halide complexes, as has been recently reported by Van Koten and coworkers.¹⁰

We are grateful to Todd Foust for writing utility programs to separate data for simple hydrogen bonds from those for bifurcated examples, and Dr F. H. Allen for useful discussions. We thank the Spanish Ministerio de Educación y Ciencia for an F.P.U. (Becas en el extranjero) grant (to G. A.), an NSF-REU grant (for partial support of E. A. B.), and the Universities of Bristol and Missouri-St Louis for financial support.

Notes and References

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‡ All N–H and O–H distances were normalised to standard neutron diffraction determined internuclear lengths, and only those structures containing intermolecular contacts with 1.80 \leq H...Cl \leq 3.15 Å and D–H...Cl angles \geq 110° were included in subsequent analyses. Data for bifurcated hydrogen bonds were removed after the initial search using locally written programs and will be discussed in a later paper.

§ Available upon request from the Authors.

¶ No spatial normalisation corrections⁹ have been applied to these scattergrams. Such corrections, although widely recognised as appropriate, are not substantial in this case since there are few fragments for which the E–Cl...H angle (E = M, C) approaches 180°.

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Received in Basel, Switzerland, 15th December 1997; 7/09014E