

The disorder in the chalcogen atom positions can be resolved by using the relative composition of the  $[\text{Ti}(\text{C}_3\text{H}_5)_2\text{Se}_x\text{S}_{3-x}]$  species as determined from the  $^{77}\text{Se}$  NMR spectrum of the Se:S = 3:2 product (see Table III). The numerical details are presented in Table V.

The asymmetrical distribution of the occupation factors of selenium in the chalcogen atom positions E(1)–E(5) implies that the chiral molecular species  $[\text{Ti}(\text{C}_3\text{H}_5)_2\text{Se}_3\text{S}_2]$  (4),  $[\text{Ti}(\text{C}_3\text{H}_5)_2\text{Se}_4\text{S}]$  (5), and  $[\text{Ti}(\text{SSe}_2\text{S}_2)]$  (17) may have preferable orientations in the lattice. Since in the present structure the chalcogen atom position E(5) (see Figure 4 and Table III) is richer in sulfur and in the related structures it is nearer to the transition metal than E(1) it was assumed that the asymmetric molecular species 4 or 5 (see Figure 1) will mainly have the orientation with the three- or four-atom selenium fragment starting from E(1) rather than E(5). In fact, since the occupation factors of selenium in E(2) and E(3) are equal,  $[\text{Ti}(\text{C}_3\text{H}_5)_2\text{Se}_3\text{S}_2]$  (4) and  $[\text{Ti}(\text{C}_3\text{H}_5)_2\text{SSe}_2\text{S}_2]$  (17) can only assume one orientation. It is also known that the crystal contains  $[\text{Ti}(\text{C}_3\text{H}_5)_2\text{S}_3]$  (1), even though it cannot be observed by  $^{77}\text{Se}$  NMR spectroscopy. Without the presence of

1, the occupation factors of selenium in E(2) and E(3) should be 100%. Therefore the relative amount of 1 in the crystal was estimated by scaling the occupation factors of selenium in these two atomic positions to the observed 82%. Finally, the relative amount of the chiral molecule 5 in the two alternative positions was adjusted by using the refined occupation factors of selenium in E(5). As a test of the disorder scheme, it can be noted that the occupation factors of selenium in E(1) and E(4) that have not been used to resolve of the disorder are reasonably well reproduced by this scheme.

**Acknowledgment.** We are grateful to Prof. T. Chivers for helpful discussions. Financial help from the Academy of Finland is also gratefully acknowledged.

**Supplementary Material Available:** Details of structure determination (Table 1S), anisotropic thermal parameters of non-hydrogen atoms (Table 2S), calculated hydrogen atom positions (Table 3S), and bond angles (Table 4S) (7 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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## Hydrogen Bonding in Alkylammonium Chlorometalates of the First Transition Metals

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Received July 19, 1990

A study of hydrogen bonding in alkylammonium chlorometalates has been carried out by using the Cambridge Structural Database as a source of data and a search tool. The results support a range of bonded H–Cl distances from 2.1 to 2.8 Å and indicate that the N–H···Cl angle should be 120–180° when significant H bonding is present. Hydrogen bonding by alkyl hydrogens to chloride ions is not supported by the data. The outer end of the range of H–Cl distances is a little longer than has been commonly used in the recent literature in analyzing hydrogen bonding in such structures. Bifurcated hydrogen bonds from a single hydrogen to two neighboring chlorides are possible, but hydrogen bonds from two different hydrogens on a single nitrogen to the same chloride ion are not observed. Inferring hydrogen bonding from N···Cl distances in the absence of hydrogen positions will give erroneous false positive results in a significant fraction of cases.

The existence of hydrogen bonds of the type N–H···X, where X = Cl or Br, is now well-known, and an array of structure determinations on alkylammonium halometalates attests to the importance of this bond in stabilizing a variety of structures.<sup>2–5</sup> However there occur in the literature many cases in which such bonds have been indicated or suggested when the hydrogen positions were unknown, by using the N···X distance as a guide to the existence or nonexistence of the bond. Inability to determine hydrogen positions is common in such structures and cannot always be overcome.<sup>6</sup> This study was undertaken to see whether such assignments from the N–Cl distance alone were or were not a good indication of hydrogen bonding. We have taken as a point of departure the view that if the sum of the two van der Waals radii for Cl and H is greater than the observed distance, then it is reasonable to call the interaction a hydrogen bond. To two significant figures, these numbers are usually quoted as 1.8 and 1.2 Å,<sup>7–9</sup> giving 2.9–3.0 Å as a maximum distance to be acceptable as a possible bond. Very early work<sup>10</sup> had suggested a range considerably longer than this for such hydrogen bonds, from 3.10 to 3.45 Å. Results presented here support a shorter upper limit than either of these suggestions, about 2.10–2.85 Å. However, this suggested range is still somewhat wider at the upper end than seems to have been common practice in interpreting such structures in recent papers.

In the last decade X-ray determinations of the structures of several hundred compounds of the general form  $\text{C}_x\text{M}_y\text{X}_z$  (C = a stable organic cation with some N–H hydrogen-bonding capacity; M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn, or Cd; and  $\text{M}_2\text{Y}_y$  may be a simple complex ion, a layer, a chain, or an oligomeric anion) have been reported and these structures are now part of the Cambridge Structural Database (CSD). This database was taken as the starting point for this study. The selected database is also a good one for examining the possibility of C–H···X hydrogen bonds. The existence of C–H···O and C–H···N hydrogen bonds is well established in several cases,<sup>11,12</sup> and Taylor and

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**Table I.** Distribution of Numbers of References As the Selection of the Database Progressed

metal	no. of raw contribns	no. of unedited contribns	no. after edit
V	13	0	0
Cr	14	0	0
Mn	36	13	9
Fe	64	7	3
Co	30	9	5
Ni	15	1	1
Cu	161	31	19
Zn	83	44	12
Cd	31	13	4
tot.	447	118	53

Kennard<sup>13</sup> have identified 13 possible examples of C-H...Cl hydrogen bonds in 9 different crystal structures. The assignment is not easy to make, because the shortest C-H...X distances in a structure are generally in the same range as the longest N-H...X distances assigned as hydrogen bonds; overlap of the two ranges is common.

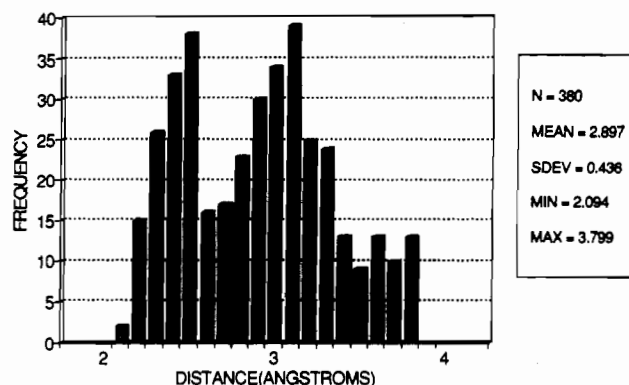
### Selection of Database

The CSD was searched for all compounds containing V, Cr, Mn, Fe, Co, Ni, Cu, Zn, or Cd linked to three or more Cl ligands (that is, bonded in the sense of crystallographic connectivity); this definition included isolated ions, layers, chains, and oligomeric ions. The presence of at least one nitrogen in the formula was required; this included all purely organic nitrogen-based cations but also picked up compounds containing chelated ethylenediamine as part of a complex cation, of which there are now a considerable number in the literature. In a few cases complexes containing three coordinated chlorides and a coordinated nitrogen were picked up by the search. These latter two classes seemed on examination of preliminary graphs to be outliers, and perhaps to bias the data somewhat. The original deck of 447 structures was edited by hand to remove these two groups of compounds, as well as all of the structures (three-fourths of the total) that for reasons of disorder or incomplete reporting did not contribute any examples of possible hydrogen bonding. This large loss reflects the number of determinations in which hydrogen positions cannot be located in structure determinations on this class of compounds. After this editing, there remained a group of 53 structure determinations, distributed as shown in Table I. Complete references for the 53 structures included are given in a bibliography (supplementary material).

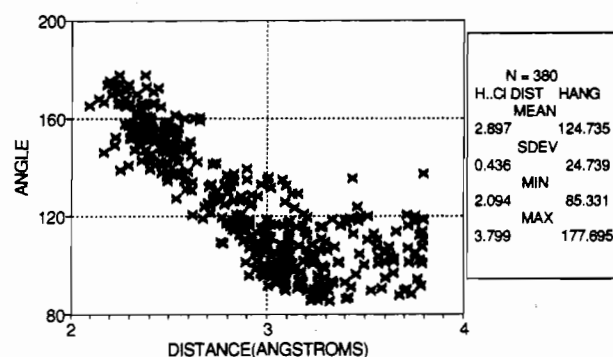
This pruned database was then searched for all C-N-H...Cl groupings, yielding a raw total of 544 examples. The CSD algorithms for this search produce a large number of duplicates, which are of two kinds: one in which one of the atoms (almost always the Cl) lies on a symmetry element and hence is calculated twice by the program logic and a second one in which the hydrogen bonding N-H has two or three carbons attached instead of only one (trimethylammonium ion is a good example). The nitrogen was required to be quaternary in this search (that is, sp<sup>3</sup> hybridized) and the attached carbon to be at least trigonal, thus eliminating aromatic ring nitrogens from the statistics but leaving anilinium-like cations. The duplicates were identified visually and removed in the final step. In the selection of the example to be kept in the type 2 duplications, the one kept was always the one with the C-N...Cl angle closest to 110°, the tetrahedral angle.

In a few cases the number of examples of the group in a single structure exceeded the program limit of 30. To avoid losing these examples, each of these structures was entered in the database twice, and in each entry about half of the hydrogens were changed to fluorine atoms. We could not find a simpler way to exceed this limit.

At the end of this process, there remained 380 examples of N-H...Cl groupings, which were analyzed in terms of four pa-



**Figure 1.** Histogram showing distribution of H...Cl distances for the 380 accepted N-H...Cl examples.



**Figure 2.** Scattergram of H...Cl distance vs the N-H...Cl angle (HANG) for the 380 accepted examples.

rameters: (1) the H...Cl distance (H-Cl); (2) the N-H...Cl angle (HANG); (3) the N...Cl distance (N-Cl); (4) the C-N...Cl angle (NANG).

The same analysis was carried out for the grouping (C,N)-C-H...Cl, yielding 1130 raw examples. We were unable to find a simple way to clean up this system and remove the duplicates. The number of duplicates is larger than 200, the limit built into the program, and we were unable to find a way to circumvent this limit for this database. Two graphs from this raw data are still presented below, since the conclusions are revealing and are not invalidated by the presence of many duplicates.

### Results and Discussion

The histogram (Figure 1) of the H...Cl distance for the first search shows a wide distribution of distances with a strong minimum of examples near 2.7 Å. The scatterplot of H...Cl vs HANG (Figure 2) shows that these short distances form an easily seen lobe for which HANG is always > 110°. The number of examples between 110 and 120° is only 11. Surprisingly, one could very nearly use the angle alone as an indicator of membership in this class; the number of exceptions, with H-Cl > 2.80 Å and HANG > 120°, is only 23. This suggests that whenever the three atoms N, H, and Cl are roughly in a straight line, there is an attractive force and the distance observed will usually be shorter than the calculated van der Waals distance. Another way to express this is to say that there is a cone of interaction about an N-H bond, with a radius of generation of about 60°; if a chloride falls within this cone it will form a hydrogen bond.

As Figure 2 shows, the distribution is continuous in both distance and angle, and there does exist a range in which the decision as to whether to call an interaction "bonded" or "van der Waals" is subjective. There are 32 examples with distances between 2.75 and 3.00 Å and HANG > 120° and 12 with HANG < 120° and H-Cl < 2.75 Å. The question of how best to divide this distribution will be discussed further below.

The N-Cl distances, in contrast (Figure 3), show no such division into short and long distances and cover a surprisingly narrow range. Moreover, a plot of N-Cl for the examples that

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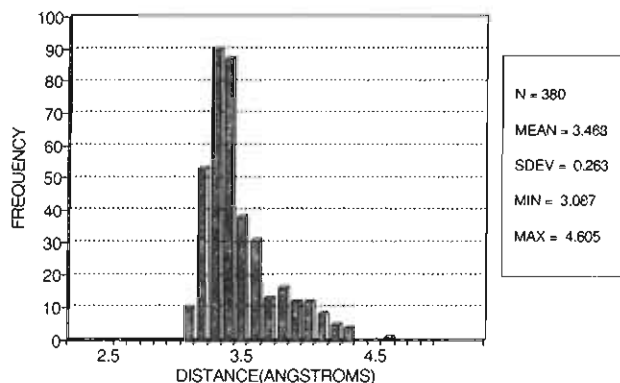


Figure 3. Histogram of N-Cl distances for the 380 accepted examples.

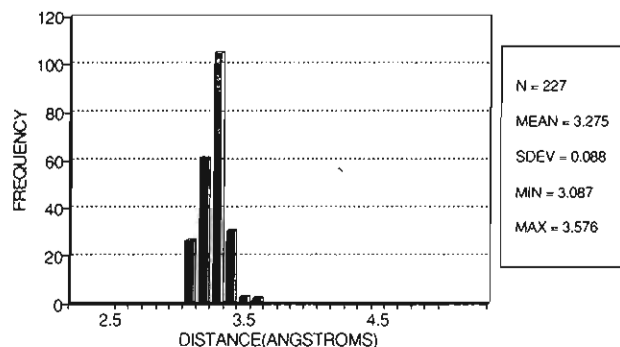


Figure 4. Histogram of N-Cl distances for the 227 examples which meet the conditions to be considered hydrogen bonded (cf. Figure 3).

fall in the "H-bond range" of Figure 2 ranges up to 3.6 Å and has almost the same mean as the unedited histogram (Figure 4). This finding underlines the uncertainty of assigning hydrogen bonds when the hydrogens have not been found in a structure determination.

It would be useful to be able to assign hydrogen bonds without the hydrogen positions; difficult structures with poor crystals will at times be done for a variety of reasons. The obvious refinement of procedure is to consider the angle C-N-Cl as well as the N-Cl distance. If the N-H-Cl angle is distributed about 180°, then the C-N-Cl angle should have a somewhat narrower range about 110°, if the nitrogen is sp<sup>3</sup> hybridized. This distribution can be easily seen in a scatterplot of H-Cl vs NANG, which is centered on an angle of 110° for the shortest H-Cl distance and broadens out rapidly as this distance increases (Figure 5). However, if one limits the N-Cl distance to 3.6 Å as suggested above and makes 85° < NANG < 135°, a considerably narrower range of angle than the limits on HANG require, the scatterplot of H-Cl vs HANG extends well beyond the identified "H-bond region". (Figure 6; cf. Figure 2). We conclude from this finding that short N-Cl distances with NANG in a reasonable range for H bonding are common, but some of them are chlorides that are packed between two hydrogens on a nitrogen but do not fall within the bonding range of either one.

#### The Most Likely H-Bond Parameters

Figure 2 can be divided into four quadrants by lines parallel to the axes at 120° horizontally and 2.85 Å vertically. The upper left quadrant represents the H-Cl interactions that are significantly shortened relative to the expected van der Waals distance, and should surely be assigned as hydrogen bonds. The lower right quadrant represents the interactions that are too long and too wide of angle to be considered as H bonds. The upper right quadrant contains those interactions that fall within the interactive cone but are constrained in some way from approaching to within a range that would be considered bonding; it may be worth noting that while the density of points in this region increases as the H-Cl distance decreases, it is still very sparse on the high side of this limit. Examples in the lower left quadrant, which contains 11 points clustered tightly in the apex, seem best described as weak

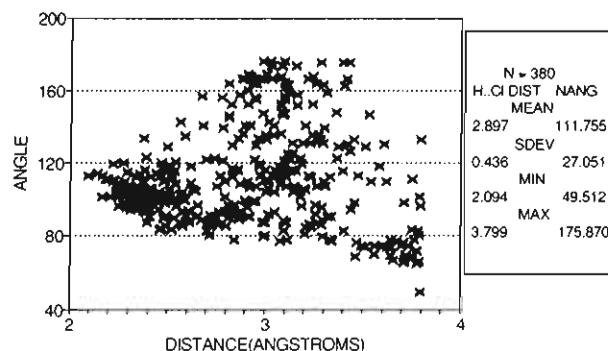


Figure 5. Scattergram of H-Cl distance vs C-N-Cl angle (NANG) for the 380 accepted examples.

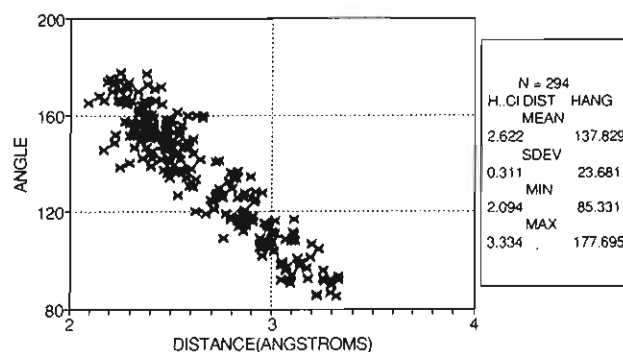


Figure 6. Scattergram of H-Cl distance vs N-H-Cl angle for examples with C-N-Cl (NANG) limited to 85° < NANG < 135° (cf. Figure 2).

hydrogen bonds at the limit of the interactive cone.

All of the papers that report distances and angles in this borderline region of the scatterplot have been examined to see if there are common factors that might account for their presence. Four of them (supplementary refs 23, 27, 34, and 46) present tables that are in excellent agreement with our observations in this study. In the four structures that report the shortest N-H-Cl distances and angles in the lower left quadrant, some kind of hidden data or refining uncertainty exists. In one case, the crystal was twinned; in another, the hydrogen positions were restrained and not refined freely; in a third, no absorption correction was made on a thin needle-shaped crystal. Since these deviant examples are only barely below the expected van der Waals distance and, in addition, have angles only slightly below 120° (three of the angles are between 117 and 119°, and the fourth is 109°), we feel that they have experimental uncertainties that include our proposed limits.

This direct examination also reveals that the tendency in assigning H bonds in these systems has been very conservative, when the hydrogen positions were known. Most of the explicitly recognized hydrogen bonds have been in the ranges 2.2–2.55 Å with bond angles at H of 150–180°. This study strongly supports a higher limit of at least 2.65–2.75 Å for an interaction to be assigned as a hydrogen bond. The angle N-H-Cl is nearly always larger than 120°, but this cannot be used as a diagnostic by itself because it is possible for a Cl atom to enter the cone of interaction but still be too far away to form a hydrogen bond, even though it does not happen very often.

This idea of the cone of interaction is strongly supported by the distribution of H-Cl distances with angle for alkyl hydrogens (Figure 7). In this scatterplot the cone of interaction, in which the H-Cl distances shorten, does not appear; the distribution of distances >2.75 Å extends over the whole range of angles, instead of being limited to angles <120°. This suggests that attractive interactions that can be called hydrogen bonds are almost absent for C-H groups but almost universal for N-H groups. There are eight C-H-Cl examples where the H-Cl distance falls below 2.75 Å; the seven papers (supplementary bibliography refs 1, 8, 33, 36, 38, 47, and 52) from which these eight examples were drawn have also been examined in detail. Five of these seven papers report either an experimental or refining difficulty or anomaly

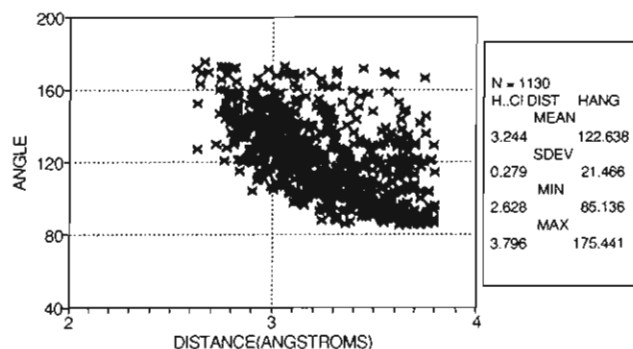


Figure 7. Scattergram of H-Cl distances vs the C-H-Cl angle for the 1130 raw examples of C-H-Cl interaction (cf. Figure 2).

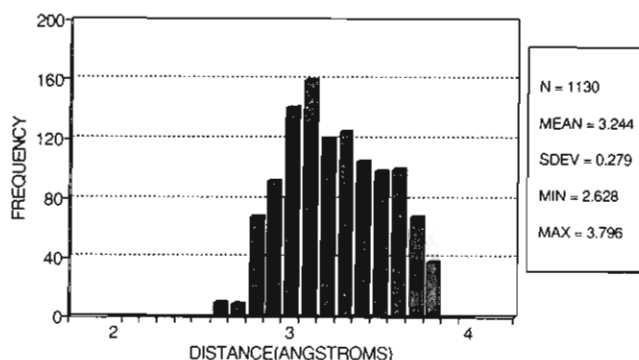


Figure 8. Histogram of C-H-Cl distances for the 1130 raw examples of C-H-Cl interactions (cf. Figure 1).

that could have led to some inaccurate C-H distances. In one case, the data were taken from a multiple twin crystal because no single crystals could be obtained; in another, the alkyl hydrogens were fixed at their calculated positions and not refined. One structure used photographic data and was only refined to an *R* of 8.5%. One made no absorption correction for a needle-shaped crystal approximately 0.1 mm × 0.1 mm × 0.7 mm and took the data with Cu K $\alpha$  radiation. One paper was accepted for publication without any details of the refinement procedure included and cannot be critically evaluated. The suggestion that these few very short distances are aberrant and in some cases erroneous is therefore very strong. Additional evidence for the rarity of C-H-Cl hydrogen bonding comes from the histogram of H-Cl

distances (Figure 8), which has a minimum distance of 2.60 Å, is sharper and narrower than the corresponding curve for N-H-Cl interactions, and shows no division into shorter and longer distances.

On the basis of these observations, we suggest that the delineated region, H-Cl < 2.75 Å and N-H-Cl > 120°, represents a region in which bonding occurs and the hydrogen and chlorine are closer than their normal van der Waals radii would allow. This is slightly more conservative than the data of Figure 2 suggest for the cutoff limit but is the best fit to the data of Figure 7. The range from 2.75 to 2.90 Å, outside this limit but inside the van der Waals distance, is an uncertain region in which H bonding may or may not occur but certainly should not be inferred on the basis of distance alone. Data on the N-H-Cl angle might well be used to support assignments in this region. Figure 6 indicates that the presence of such an interaction cannot be deduced with any confidence if only the non-hydrogen positions are known, even if NANG is taken into account. Alkyl hydrogen bonding to chloride is very rare if it occurs at all, and there are no clear examples of it in this sample of data. Of Taylor and Kennard's<sup>13</sup> 13 examples of C-H-Cl bonds, five would be classed as bonded with our criterion; all five of them occur in amino acid structures. Several of the others are bonds to organically bound chlorine and are probably not comparable to those of the compounds in our sample.

Two other consequences of this study are of interest. First, it is quite possible for one hydrogen to bond to two different chloride ions in a structure, because two chlorides within a van der Waals distance of each other can easily enter the same cone of interaction. That is, bifurcated hydrogen bonds are reasonable. Second, two hydrogens on the same nitrogen cannot form hydrogen bonds to the same chloride; a chloride ion symmetrically placed between two hydrogens on a tetrahedral nitrogen and 2.8 Å from each will subtend an angle of about 105° at the hydrogen, below the allowable minimum of 120°. The database was searched for both of these configuration; 27 examples of the first were found, but none of the second.

**Acknowledgment.** K.E. wishes to thank the Fulbright Foundation and The Gobierno Vasco for fellowships that made possible his stay in Spain to carry out this research. We are also indebted to a reviewer for calling our attention to the work by Taylor and Kennard.<sup>13</sup>

**Supplementary Material Available:** A bibliography of 53 references used in this study (4 pages). Ordering information is given on any current masthead page.