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Notes

Is the “Unusual” Three-Center D−H---A−M Hydrogen Bond Really Unusual?

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Introduction

Yap *et al.*[1] recently described as “unusual” the three-center hydrogen bond they found in the structure of 2,6-diphenylpyridium tetrachloroaurate (**1**) (Chart 1). This description was presumably based on the assumption that the three-center hydrogen bond, represented in general by **2**, is not common in organometallic complexes.

Recent attention to the general nature of the “three-center hydrogen bond”,[2] its presence in nitroanilines[3] and in carboxylic acids,[4] and our own work in this area[5] attracted our attention to this paper. Moreover, Etter’s pioneering work on the definition and identification of hydrogen bond patterns using a convenient graph set notation[5] made **1**−**3** recognizable as simply three representatives of the generic $\mathbf{R}_1^2\mathbf{(4)}$ pattern,[6] where the designation indicates a ring pattern containing four atoms, including one donor and two acceptors.

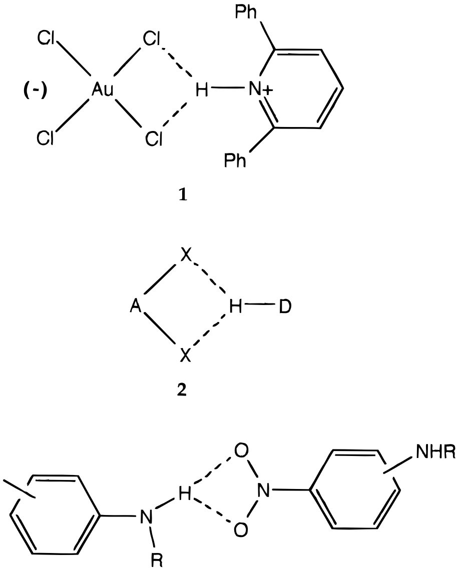
The Cambridge Structural Database (CSD) may be readily searched for intermolecular interactions such as $\mathbf{R}_1^2\mathbf{(4)}$ to identify the mere existence of particular patterns, their frequency, and, when patterns cross the bounds of traditional chemical functionality, the chemical diversity of a pattern as a representative of a particular *hydrogen bond functionality*.

These lines of reasoning prompted a study in response to the statement in ref 1 about the unusual nature of **1**. We report here on the results of that study.

Results

We carried out a search of CSD (version of Oct 1995)[7] on the generic $\mathbf{R}_1^2\mathbf{(4)}$, **2** (where A = any atom, X = acceptor, D = any atom); the H---X distance was limited to 3.0 Å. This search resulted in 28 968 observation of the pattern occurring in 9073 different crystal structures (“hits”, in the jargon of the CSD), suggesting that the pattern is anything but unusual. However we narrowed the search to a case more akin to that noted in ref 1 as in **4**.

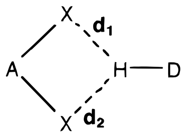
Chart 1



1

2

3



X = any atom except N, O

A = any atom, D = N, O

4

This limits us to 1309 observations for 620 hits. In a plot of d_1 vs d_2 (Figure 1) it is seen that there is considerable scatter in these points, although there is clearly a large concentration of observations with $d_1 = d_2$, which most nearly approximates the $\mathbf{R}_1^2\mathbf{(4)}$ pattern. We therefore further limited the search to $|d_1 - d_2| < 0.3$ to concentrate on the essentially symmetric observations. With these limitations we now obtain 607 observations for 387 hits where M is Cu, Z, Sn, Te, Co, Hg, Mo, Sb, Mn, Pt, Ru, Au, Pb, Re, Ir, Ti, Ca, Cd, Cr, P, Al, Si, or W. The observations were limited to four acceptors A: Cl, F, Br, and S. For direct comparison with the example of ref 1 we limited D to nitrogen. From the results summarized in Table 1 it is clear that the $\mathbf{R}_1^2\mathbf{(4)}$ pattern, of which **1** is but one example, is by no means “unusual”.

To examine the metrical details of the resulting $\mathbf{R}_1^2\mathbf{(4)}$ case we normalized the N−H bond distance to 1.033 Å along the vector of the experimentally reported hydrogen pattern.[8] The results are summarized in Table 2.

We divided this pattern into four cases in which the acceptors are Cl, F, Br, or S; in each case the bond lengths to hydrogen were normalized to N−H = 1.033 Å according to the standard

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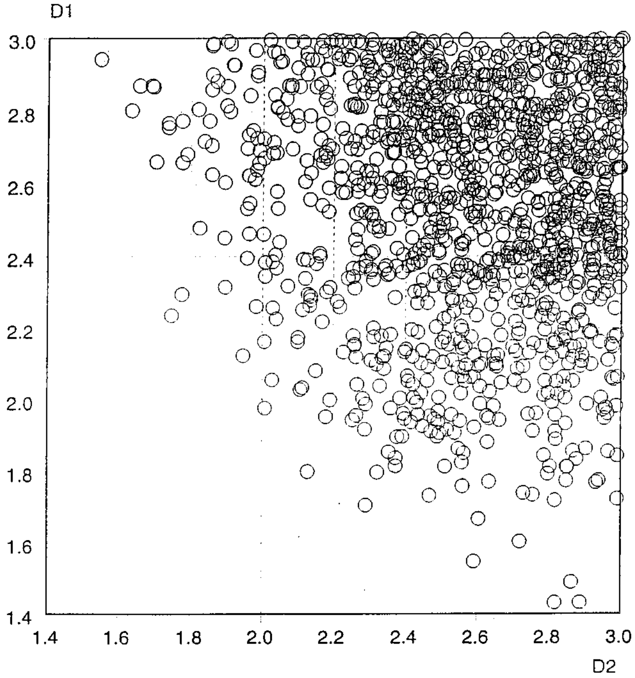

Figure 1. Scatter plot of distance d_1 *vs* distance d_2 for the 1309 observations of **4** (d_1, d_2 < 3.0 Å).

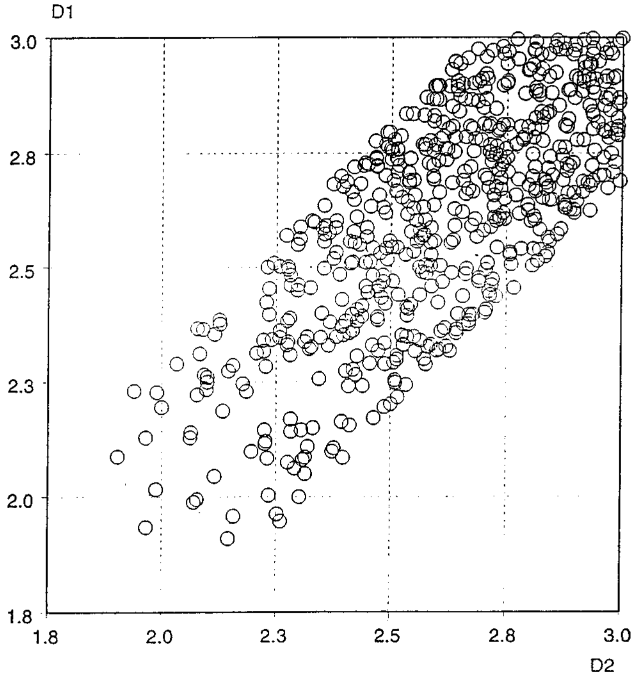

Figure 2. Scatter plot of distance d_1 *vs* distance d_2 in **4** ($d_1 - d_2$ < 0.3 Å).

protocol.[8] We summarize the results here for each of the four specific acceptor groups in Tables 1 and 2 with a typical example shown in Figure 3.

The Acceptor Is Cl. The typical range in the two center hydrogen bonds is 2.91−3.52 Å. The case here deals with a the three-center bond, but the values still fall into this range. The average distance for N---Cl is 3.4(1) Å while that for Cl---H is 2.66(13) Å. These are both shorter than those in ref 1, where N---Cl is 3.65 and 3.45 Å and Cl---H is 2.75(8) Å.

The average M−Cl---H angle is 82.4°, and the angles found by Yap *et al.* in their structure is larger at 90(3)°. According to those authors an M−Cl---H angle of 90° is favorable for H bonding probably because of the higher basicity of p-type Cl lone pair relative to the sp lone pair.[1]

Table 1. Observations/Hits of the $\mathbf{R_1^2(4)}$ pattern from the CSD[a]

$d_1 - d_2 < 0.3$ Å	Hits/Observations	
387/607	620/1309	A X A
177/242	272/433	Cl X Cl
184/334	311/827	F X F
13/13	16/18	Br X Br
10/15	18/28	S X S

[a] See text for details of column headings.

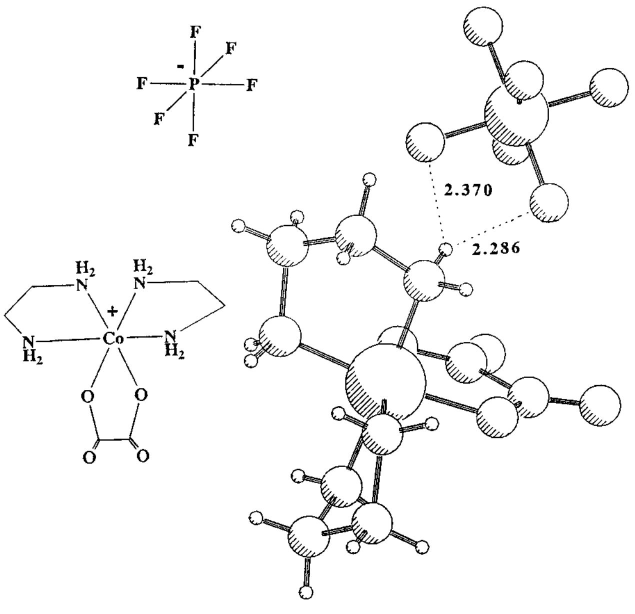

Figure 3. Typical example of the $\mathbf{R_1^2(4)}$ pattern **4** (D = N, A = P, X = F) from the CSD search. The REFCODE [7] is LIGLOC. The structural formulas are shown together with a PLUTO plot of of the actual structure.

Table 2. Average Distances and Angles and ESD's for D = N and Observations in Table 1

X				
Br	S	Cl	F	param
3.52(0.12)	3.43(0.05)	3.40(0.10)	3.10(0.12)	N---X
2.76(0.13)	2.57(0.11)	2.66(0.13)	2.35(0.28)	X---H
84.1(5.9)	79.9(5.5)	82.4(6.8)	93.7(9.8)	M−X--H

The Acceptor Is F. The distances N---F are 3.10 Å, and N−H---F is 2.35 Å (Table 2). The distances are shorter than those of acceptor Cl, which is not unexpected from the relative sizes of the atoms. The angle M−F---H found to be 93.7° is larger by ∼1.2σ than those when the acceptor is Cl but closer to the angles found by Yap *et al*.

The Acceptor Is Br. The distances when Br is acceptor tend to be slightly longer; N---Br is 3.52(12) Å, and Br---H is 2.76 Å. The mean M−Br---H angle is 84.1°, within one esd of those for Cl and S and smaller than for F by one esd of the value for the latter.

The Acceptor Is S. The results for acceptor S are essentially the same as for Cl as acceptor: N---S is 3.43 Å and S---H is 2.57 Å. The mean angle M−S---H is smaller by 1.4σ than that found for F.

Conclusion

The $\mathbf{R_1^2(4)}$ pattern, in which the acceptor is M−X and the donor H−D, is not particularly unusual; on the contrary, it can be found in many structures with a wide variety of chemical functionality. The apparent limitation when X is not N or O is that X = F, Cl, Br, or S with many possibilities (metallic or non-metallic) for M, the atom bonded to the two acceptor atoms.

We believe that there are many more patterns of common-hydrogen bond functionality, incorporating a wide variety of chemical functionality. The use of graph set notation in common with the data and tools from the CSD will help to recognize and characterize them.

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