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Further ‘tours’ of the CrystalEye system

Chemical and Geometry Search.

Let us assume that we are interested in arsenic-chlorine bonds (As-Cl).

Figure 1 Performing a chemically-based search (left) and the displayed results of that search (right)

The CrystalEye system has been pre-indexed to calculate all bonds between all atoms within covalent bonding distance, and in this case reports 26 articles containing As-Cl bonds. Taking the third article (Spinney, Korobkov, & Richeson, 2007) as an example, and following the ‘Moieties’ link from the summary page, we see the view of the moiety:

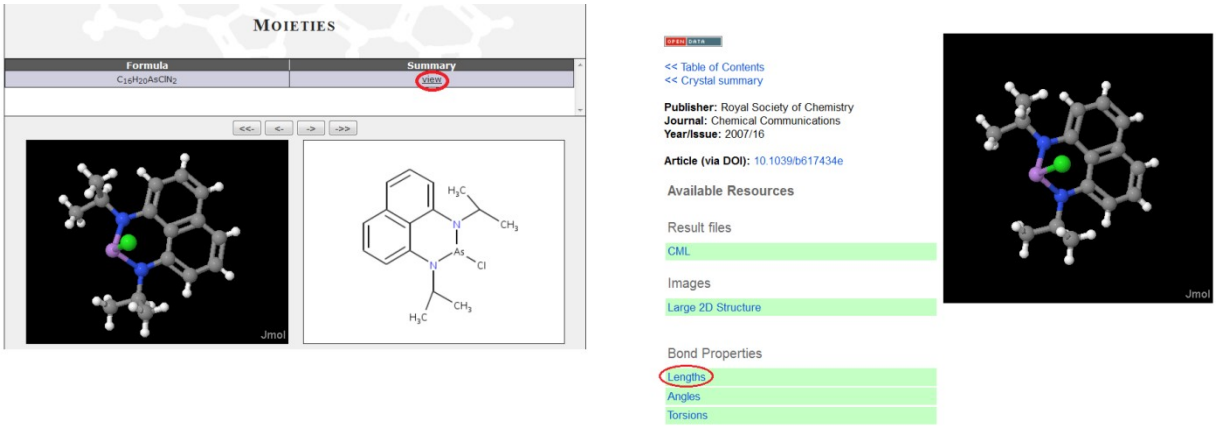

Figure 2 CrystalEye lists the calculated moieties (left), which each have individual summary pages (right).

The molecular geometry is examined by following the ‘Lengths’ link under ‘Bond Properties’ (circled in Figure B2), which tabulates all bond lengths between covalently bonded atoms.

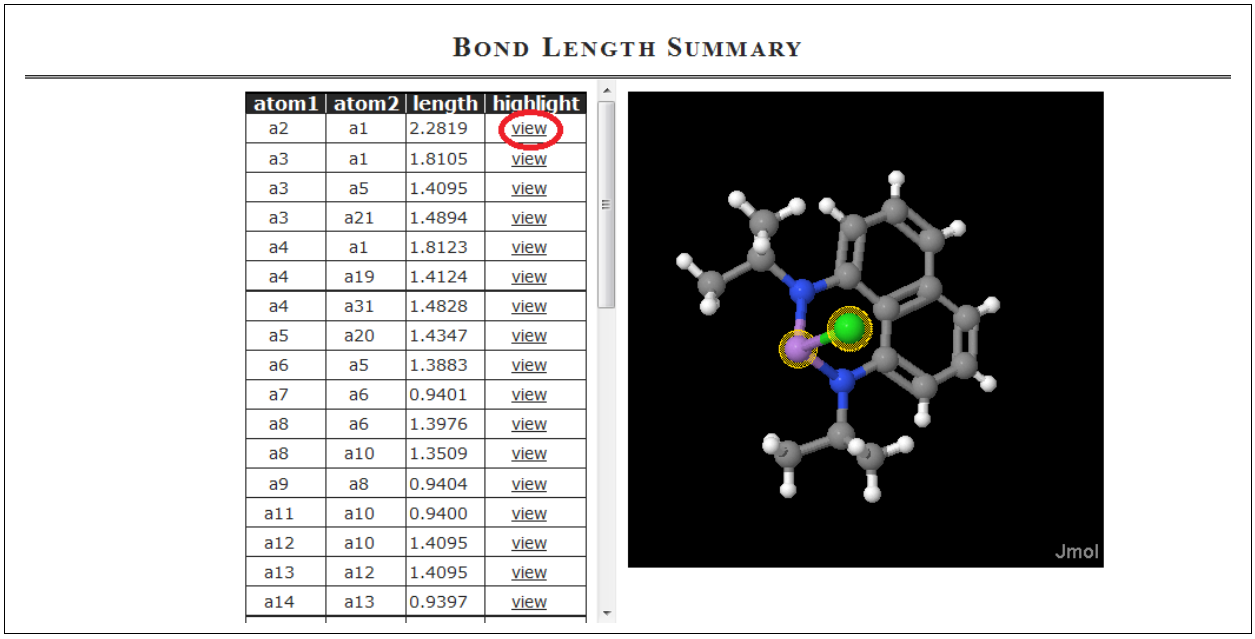

Figure 3 The molecular geometry (bond lengths) of the moiety. The 'view' hyperlink highlights the atoms forming the bond in question (the As-Cl bond).

There are similar compilations of bond angles and torsion angles.

Bond Length Search

We can systematically browse the molecular geometry of As-Cl compounds because every bond length in the CrystalEye system (>10 million) has been indexed. We can select any pair of atoms, in our case As, and tabulate all the elements which are known to form covalent bonds:

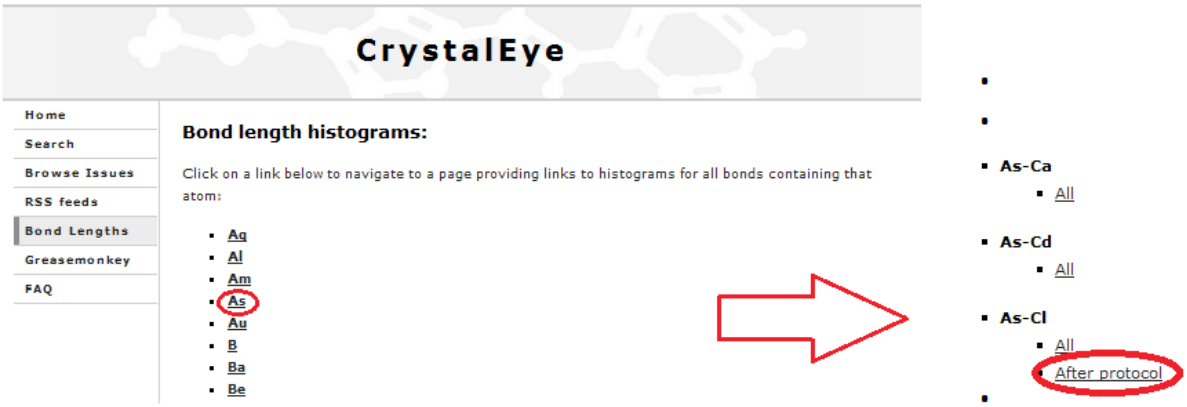

Figure 4 (Left) Using the 'Bond Length' menu to investigate bonds between specific pairs of atoms (in this case arsenic, As, and chlorine, Cl). Following the As-Cl 'after protocol' hyperlink (circled, right) generates a histogram of bond lengths.

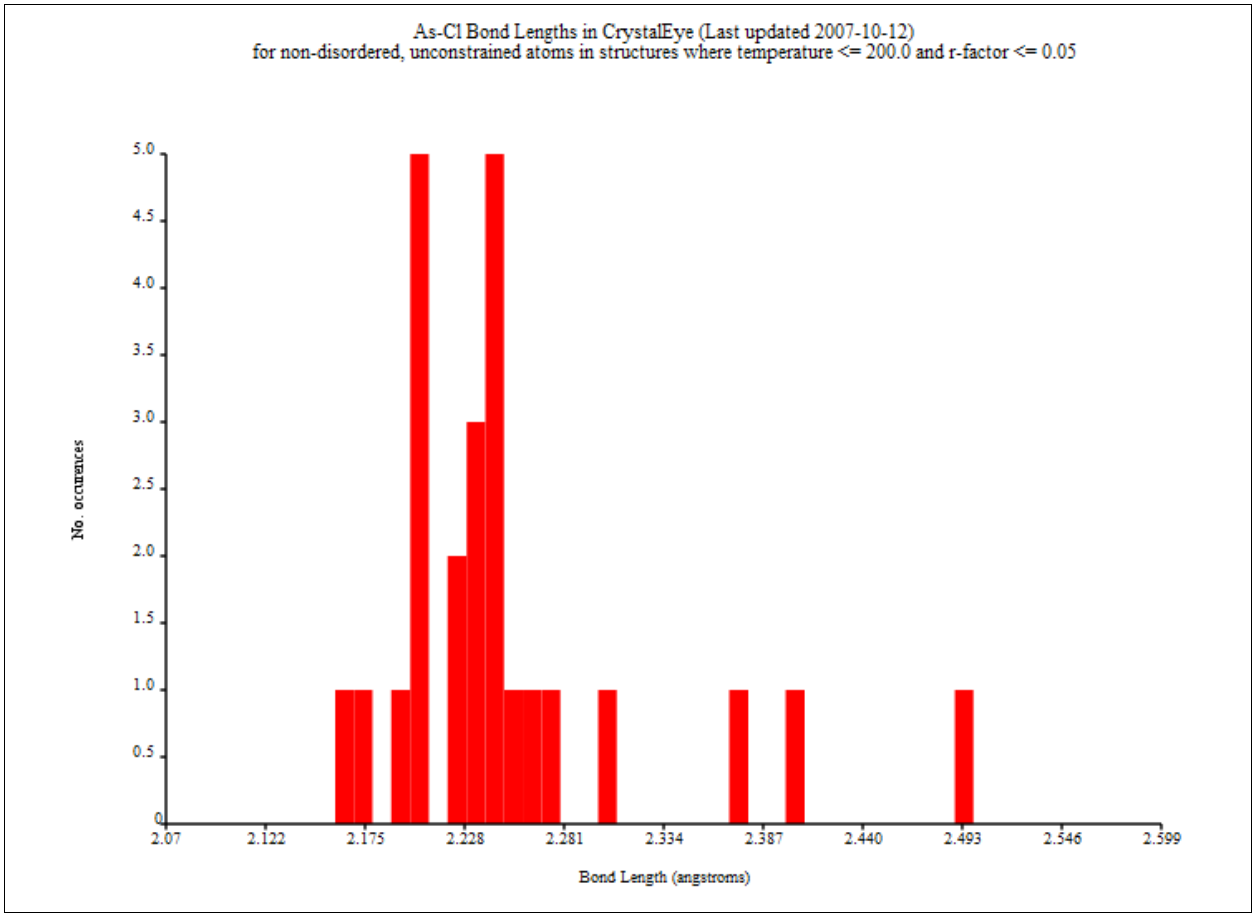

Figure 5 The 'after protocol' histogram generated for As-Cl bonds, comprising only the most accurately determined structures (*i.e.* those fulfilling the conditions elucidated in the histogram title).

The previous structure was an unexceptional bond length (2.2819Å) for As-Cl. We may however be interested in the extremes, and try to interpret these in chemical terms. The leftmost bin (shortest As-Cl bonds) of the histogram reveals two structures, both containing the $AsCl_3$ molecule.

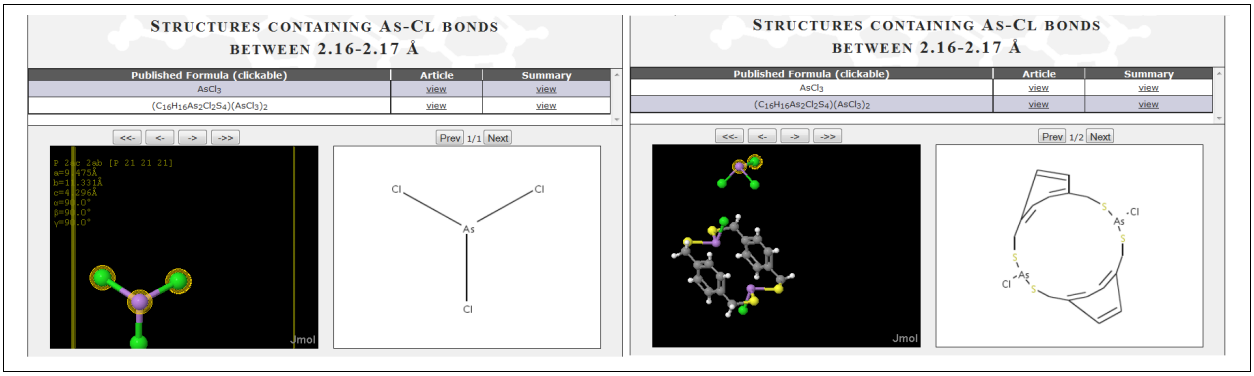

Figure 6 a) $AsCl_3$ at various temperatures (Galy, Enjalbert, Lecante, & Burian, 2002) (left); b) A structure (Vickaryous, Healey, Berryman, & Johnson, 2005) containing several As-Cl; it is the bond in the free $AsCl_3$ molecule that is particularly short (right).

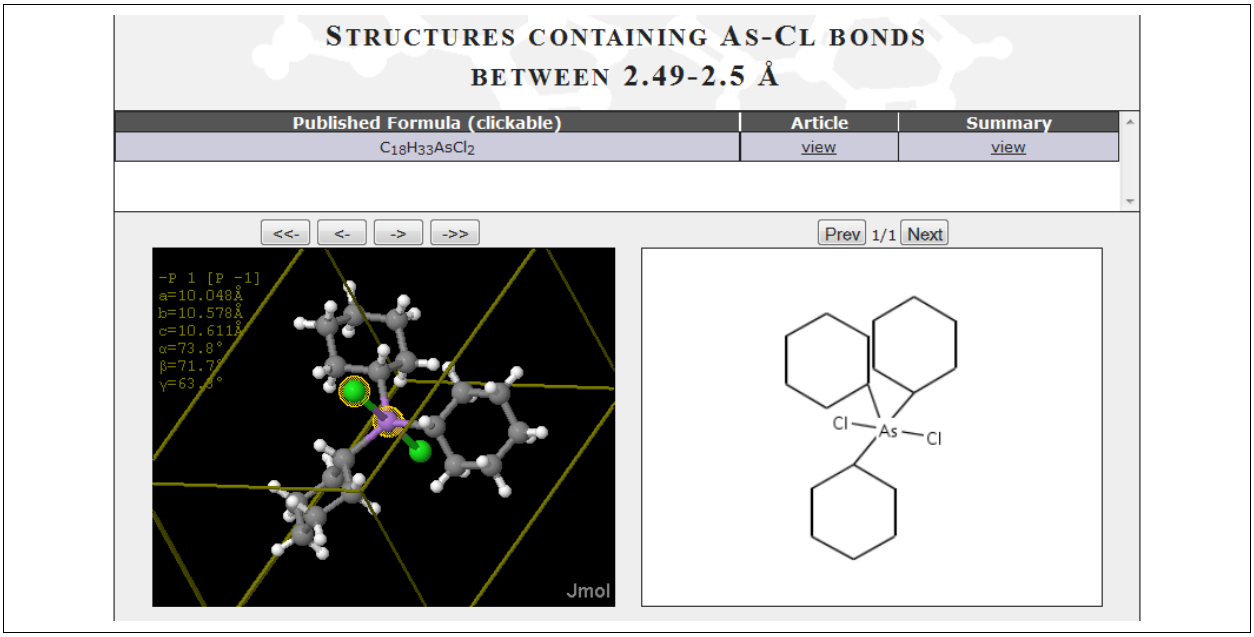

Figure 7 A similar search for very long As-Cl bonds (the rightmost bin of the histogram) reveals a penta-coordinate As (Pascu, Silaghi-Dumitrescu, Blake, Li, Haiduc, & Sowerby, 1998) where the axial As-Cl bond (highlighted) is shown to be of extreme length.

Although none of these bond lengths is surprising (the increase in length with coordination number and axial substitution is well known), it is a simple and dramatic illustration.

Disorder and Inorganic Structures

The next tour shows some of the features associated with inorganic structures and disordered structures.

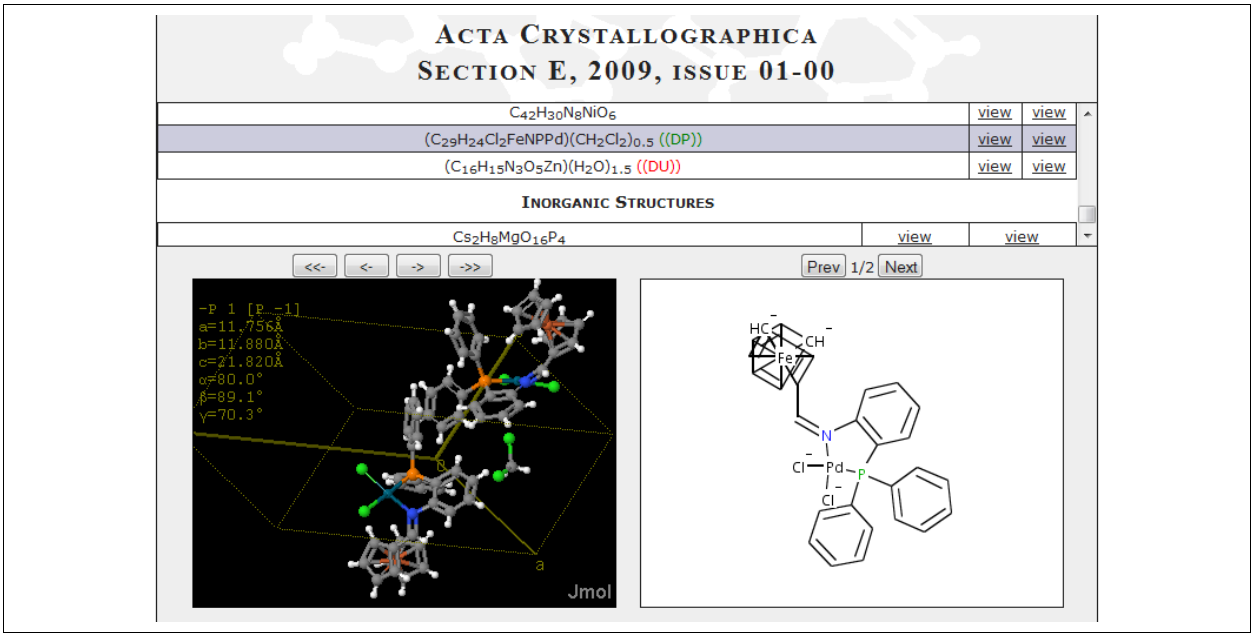

Figure 8 CrystalEye has identified this structure as being disordered (indicated by the ((DP)) after the formula).

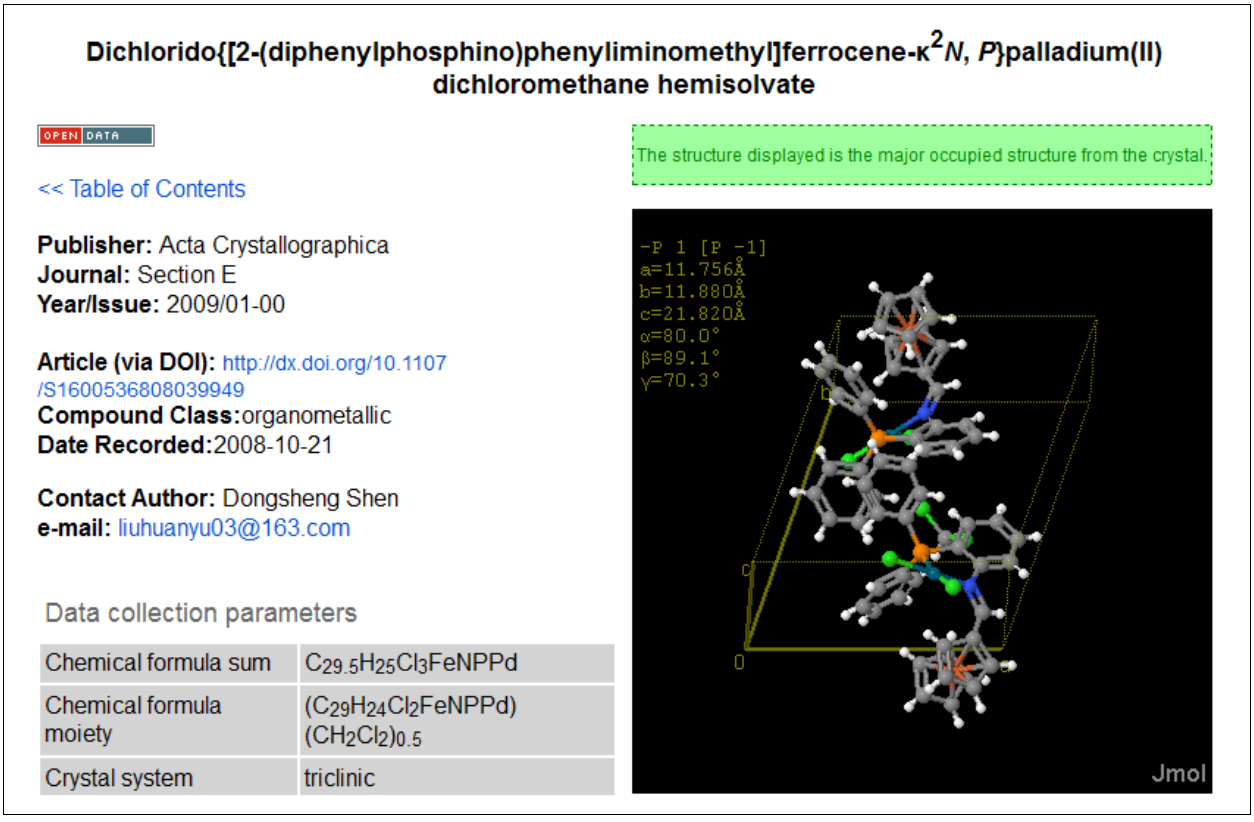

Figure 9 CrystalEye has successfully analysed the reported disorder and shown the atoms and connectivity represented by the major occupant of the crystal.

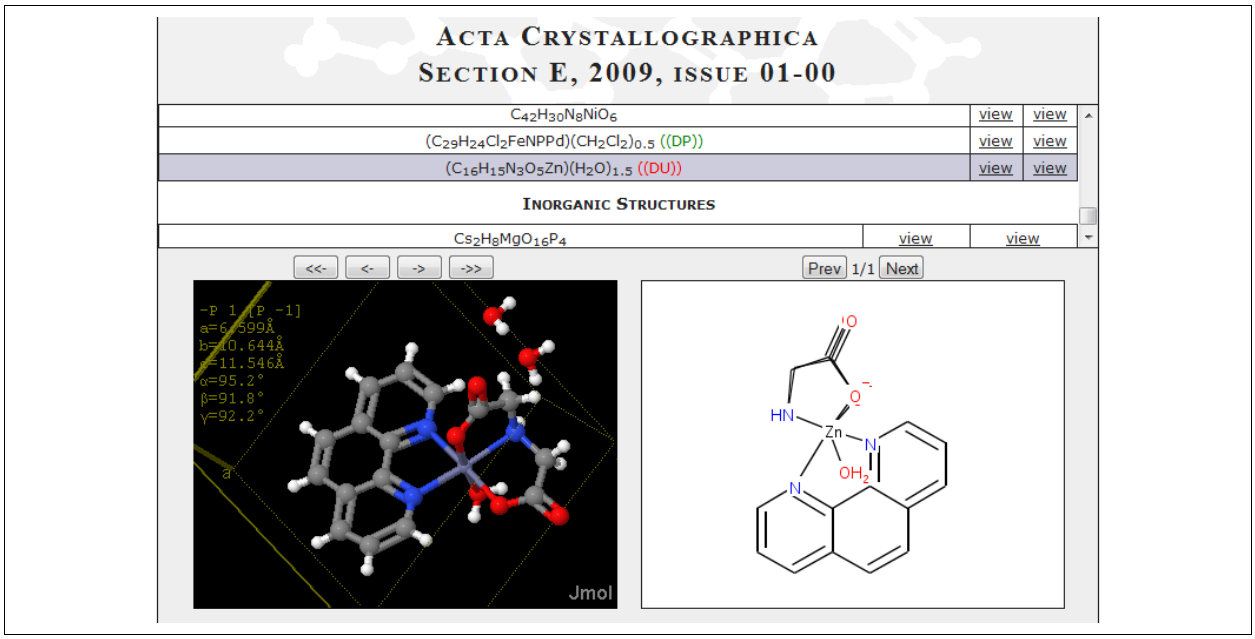

Figure 10 CrystalEye has detected that there is disorder in the structure (either because the atoms have fractional occupancies or because the authors have reported disorder using the CIF mechanism).

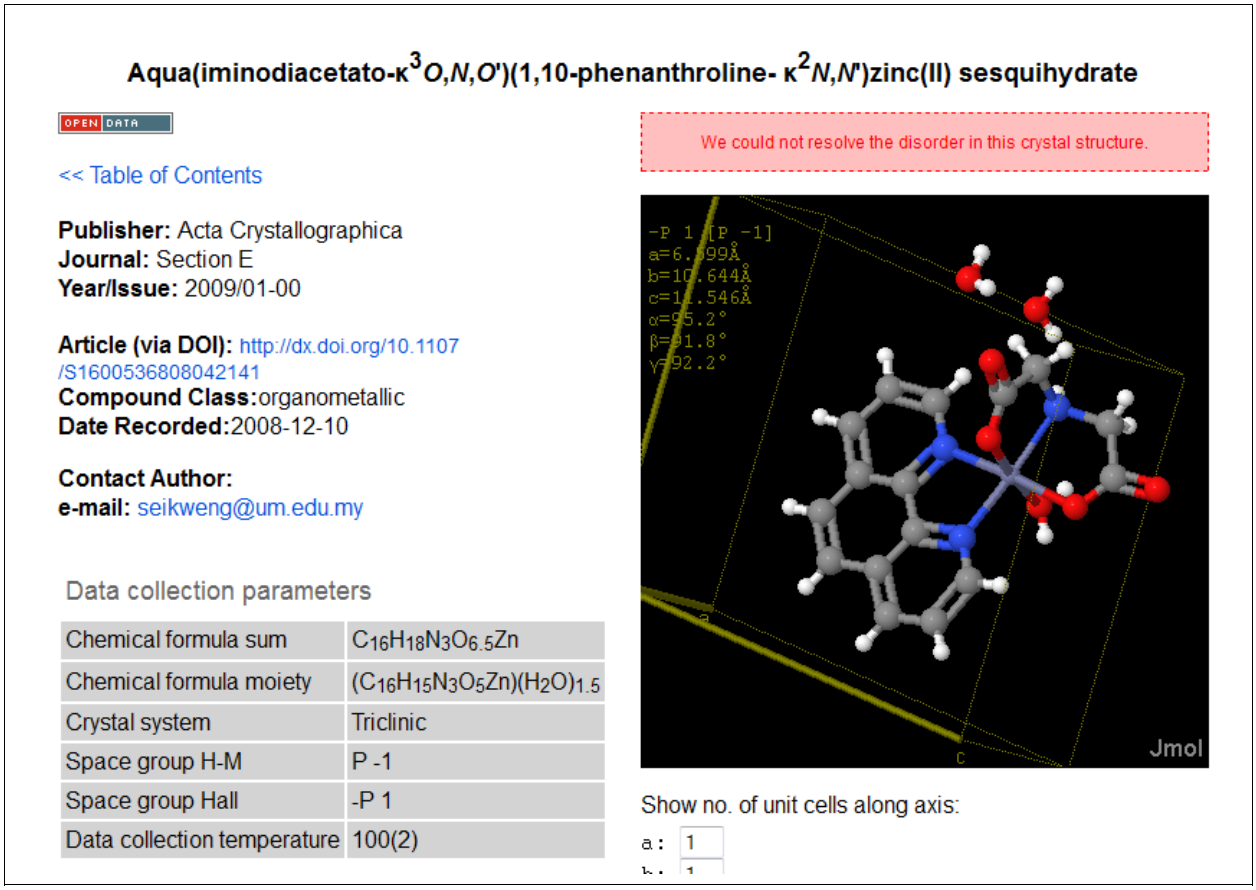

Figure 11 CrystalEye announces that it has done its best to interpret the disordered structure but that readers should beware.

For many inorganic structures the connection table representation and crystallochemical unit contents are inappropriate, and instead CrystalEye builds the complete unit cell as the default display.

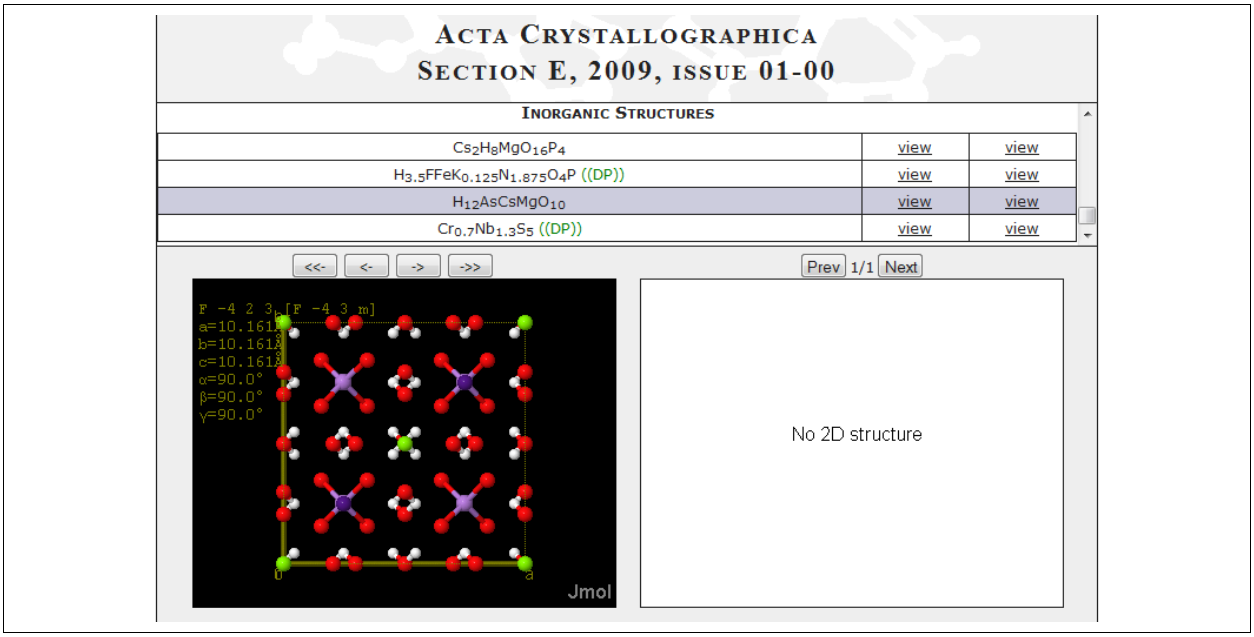

Figure 12 CrystalEye displays the complete unit cell by default when unable to build a connection table representation ('No 2D structure'). The sub-components of the structure are easily visualised (caesium ions (blue), magnesium (green) and arsenic (purple)).

Fragments

We select an organometallic structure and explore the fragments from which it may be constructed.

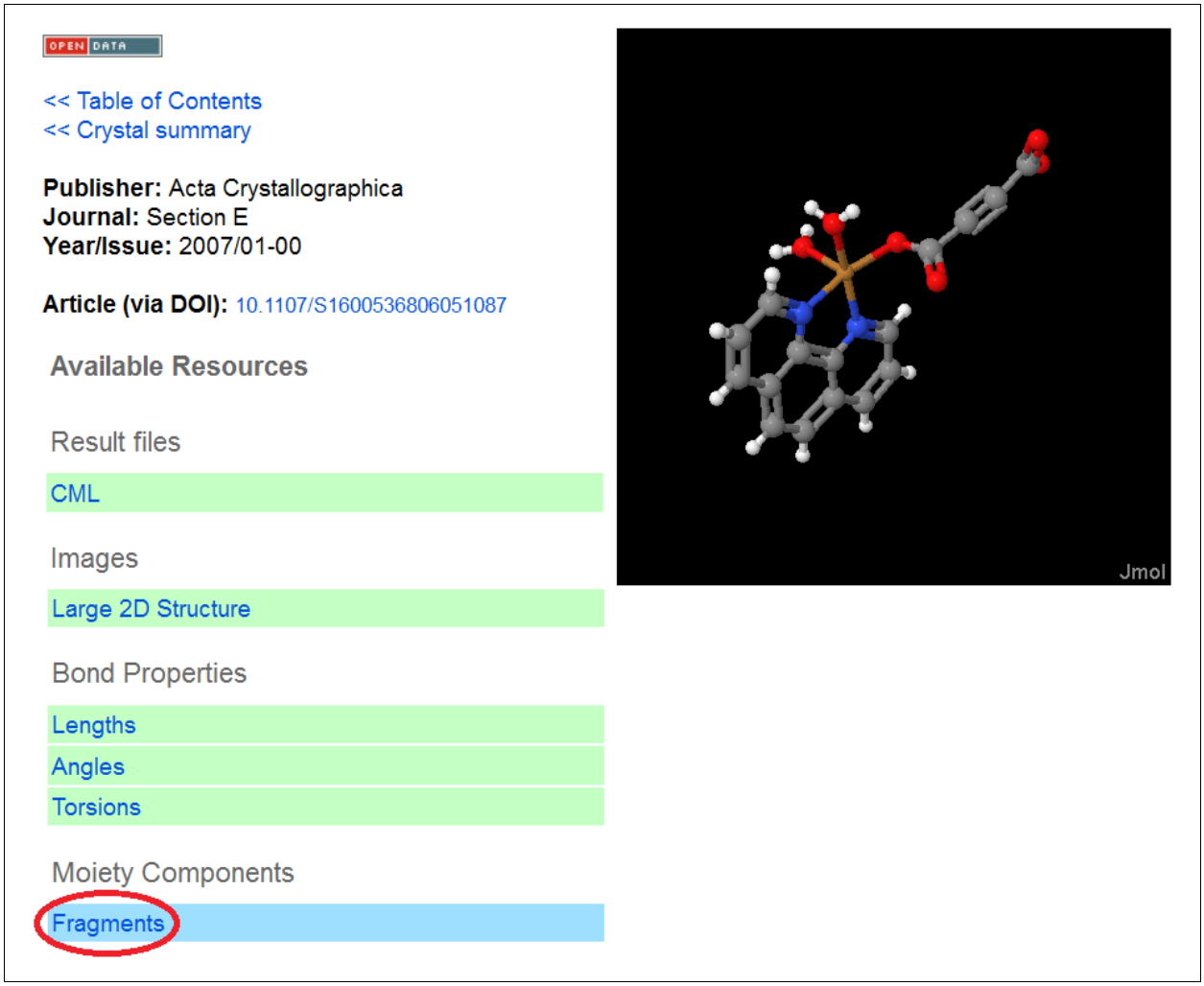

Figure 13 From the moiety summary page we follow the 'Fragments' link (circled) which lists ligands, ring nuclei and metal centres. These fragments can be viewed and the bond lengths and angles examined in the same way as for moieties.

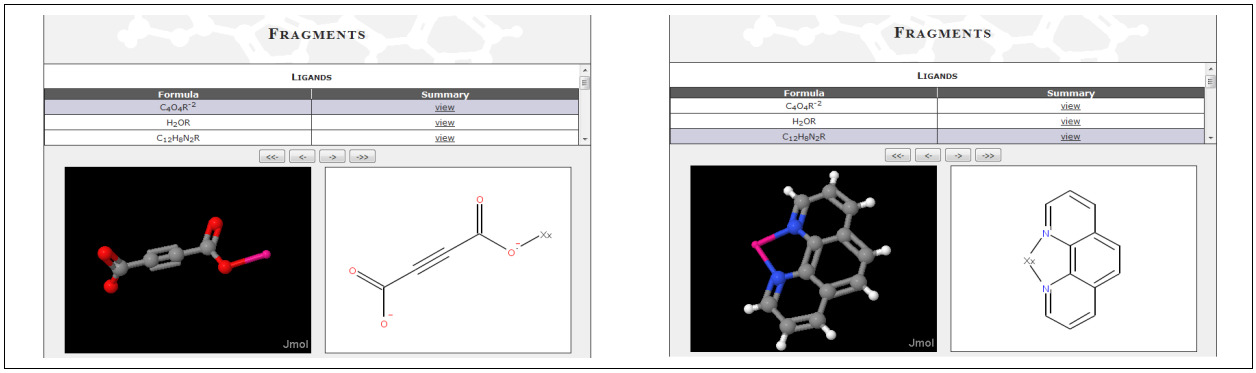

Figure 14 The fragment page in this case lists three ligands. The first is the acetylene-dicarboxylic group (left) where one acid group is negatively charged and the other is bonded to the metal. Broken links in the fragment are shown by a pink bond with a small dummy atom (Xx). The

second ligand is a metal-coordinated water (not shown) but the third ligand (right) is a coordinated 1,10-phenanthroline system.

These components can be used either for analysing molecular geometry or as Lego™-like building blocks to create hypothetical new complexes. The value of using such fragments is that they are likely to be close to experimental geometries in the target, and do not rely on approximations in force-fields or QM calculations.

The second fragment type in this moiety comprises the ring nuclei, and in this case there is just one – the phenanthroline system.

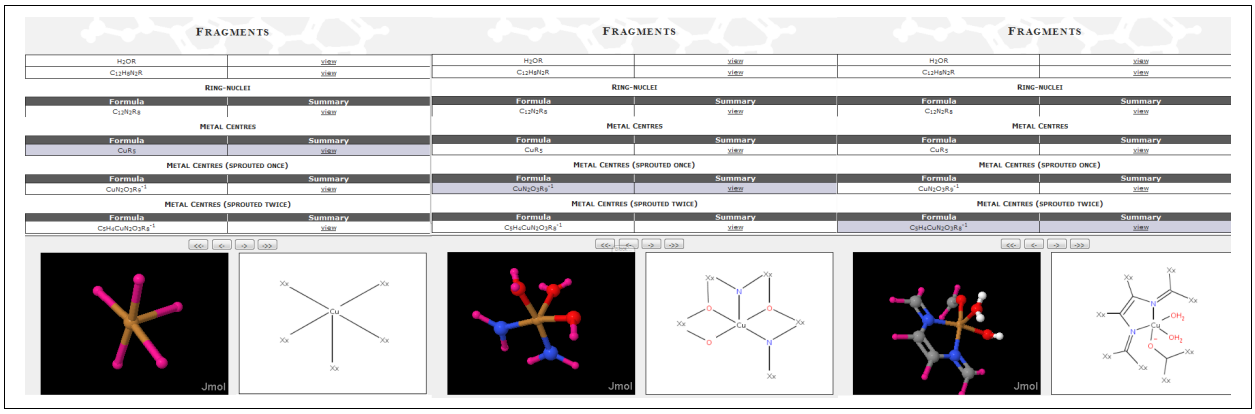

Figure 15 The third fragment type is metal centres, where CrystalEye analyses the environment around each metal. Here we can see the first coordination sphere (CRU5, a slightly distorted square pyramid; left), the next coordination sphere (centre) with two water molecules, two planar nitrogen ligands and an oxygen ligand (in these depictions the further coordination sphere is shown by pink bonds and dummy atoms). The next level of coordination (sprouted twice; right) shows enough of the chemistry that this would act as a useful template for building or model on which calculations might be based. In multi-ring structures CrystalEye will break the structure down into several ring nuclei.

CrystalEye fragments also describe chains - linkers between ring nuclei (not shown) and metal clusters.

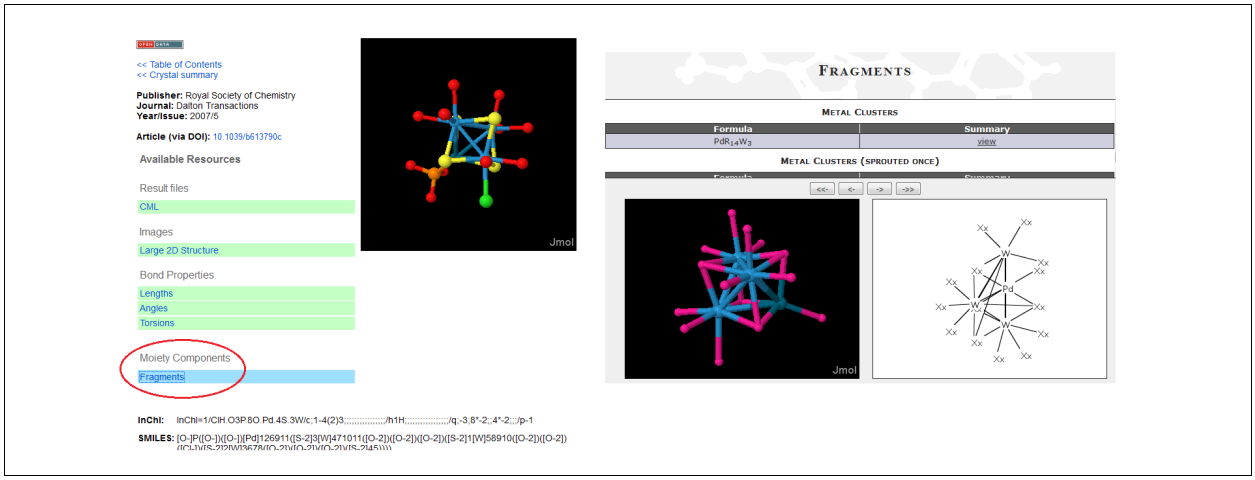

Figure 16 This moiety has been identified as containing a metal cluster fragment, in which the metal environment is explored as a clustered object where there are no common ligands other than halogens and heavier elements.