

Towards supramolecular inorganic chemistry

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Abstract. Structural interest in organometallic and cluster compounds has been largely confined to their molecular structure and stereochemistry; their crystal structures and molecular packings have not been studied seriously. However, the extended structure contains information on intermolecular interactions which may be utilized for supramolecular assembly.

Keywords. Cluster compounds; stereochemistry; organometallic compounds.

1. Introduction

There has been a surge of interest in recent years in supramolecular chemistry; that is, chemistry beyond the molecule (Lehn 1990; Vögtle 1991). Central to the theme of this subject is the fact that molecules may be assembled with weak intermolecular interactions to give supermolecules whose properties are characteristic of the supramolecular rather than the molecular structure. The molecular crystal, whether of a single component or consisting of different components, is one of the best examples of a supermolecule (Dunitz 1991) because molecules are assembled through a process of mutual recognition in very precise ways, obeying the geometrical dictates of close-packing and the orientational requirements of weak intermolecular interactions such as hydrogen bonding. The factors governing the adoption of particular types of organic crystal structures are beginning to be better understood and several contributions have appeared in this area (Kitaigorodskii 1973; Desiraju 1989; Kalman and Hargittai 1993).

In contrast, the rules governing the crystal packing of organometallic and cluster compounds are still to be established. While the Cambridge Structural Database (CSD) (Allen *et al* 1991) is a database which contains all crystal structures of "organic" carbon (that is, excluding carbides, carbonates, cyanides etc), more than 50% of the 109,000 odd structures in the April 1993 version of the CSD represent molecular inorganic compounds. The CSD is therefore a valuable storehouse of information on the packing characteristics of inorganic compounds. In spite of this, the almost exclusive interest of inorganic structural chemists and crystallographers has been in the *molecular* structure and stereochemistry of these clusters and organometallic compounds rather than in their *crystal* structures and molecular packing. The priorities of organometallic crystallography today are therefore comparable to those of small-molecule crystallography in the sixties and early seventies.

Of course, many factors which influence and guide organic crystal packing are also important in the crystal engineering of organometallic compounds. This is because the metal centres in these compounds are often situated in the molecular cores and are

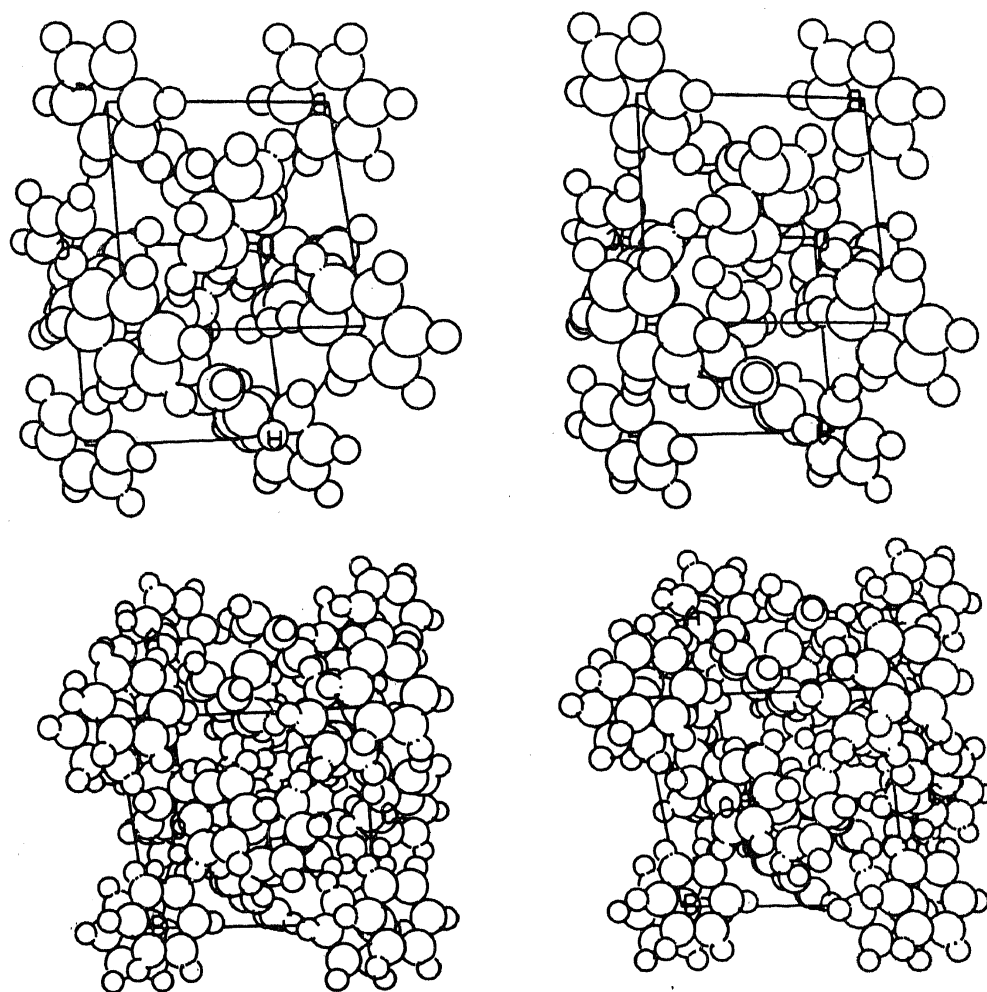


Figure 1. Stereoviews of the crystal structures of benzene (top) and dibenzenechromium (bottom) to show the essential similarity in the packing arrangement in the two structures.

well-shielded from neighbouring molecules. Effectively, the outer portions of these molecules – the rims or peripheries are “organic” in nature. Since these peripheries are the crucial ones in determining crystal structures, the packing problem reduces to the organic case. An illustrative example is obtained when one compares the crystal structures of benzene (Bacon *et al* 1964) and dibenzenechromium (Keulen and Jellinek 1966). These structures are shown in figure 1. The benzene molecule is quasi-spherical or discoid in shape and adopts a quasi-face centred cubic structure (actually orthorhombic with nearly equal cell edges). Dibenzenechromium is more nearly spherical; accordingly the space group is now accurately cubic but still quasi-face centred because the tilting of neighbouring molecules permits the formation of herringbone C...H interactions. What is interesting is that the Cr atoms are well-screened and play a negligible role in stabilizing the crystal structure of dibenzenechromium.

2. Au...Au interactions

There are cases, however, where metal-atom interactions play a part in determining crystal structures. In these cases, the metal atoms must necessarily be well-exposed

and be able to participate in stabilising interactions. A case in point is the Au...Au interaction which has been studied theoretically and experimentally (Jones 1986; Schmidbaur *et al* 1988; Pyykko and Zhao 1991). It is believed that this "aurophilic" interaction is caused by relativistic effects. The interaction has a pronounced influence on structure and stereochemistry. We have studied the geometrical properties of this interaction using the 693 Au-containing crystal structures in the 1990 version of the CSD (Pathaneni and Desiraju 1993a).

The main conclusions of this work are as follows:

(a) For compounds of the type X–Au–Y, the Au...Au distance is in the range 3.25–3.85 Å and the X(Y)–Au...Au–X(Y) torsion angle lies either around 0° (eclipsed) or 90° (staggered). Figure 2 shows this Au...Au contact in a typical structure, (2-phenylethynyl) (triphenyl phosphine) gold (I), Au(C≡CPh) (PPh₃), (CSD refcode DUZYUS; Bruce and Duffy 1986). It may be seen from figure 2 that the Au...Au contact is staggered. The eclipsed contacts are generally longer and the staggered ones shorter suggesting a steric factor but, unusually, some of the eclipsed ones are among the shortest found in this study. This suggests that other factors such as softness of the X and Y groups may be important, the softer ligand giving a shorter Au...Au contact (Pyykko *et al* 1993). The formation of an Au...Au \angle contact deforms the X–Au–Y angle from linearity with the X–Au–Y fragment being "pinched" towards the approaching Au atom and so the contact may be likened to an incipient Au–Au bond as has been described in the principle of structure correlation (Burgi and Dunitz 1983).

(b) For higher clusters, there are a large number of short Au...Au contacts in the range 2.70–3.40 Å (the Au...Au distance in the pure metal is 2.89 Å) and larger the number of contacts within a cluster, the shorter the mean Au...Au distance. In the limit, as the structure tends towards Au⁰, the stabilisation through Au...Au interactions becomes greater. In all this, we are only restating the well-known fact that in most chemical systems, elemental gold is favoured thermodynamically over its compounds.

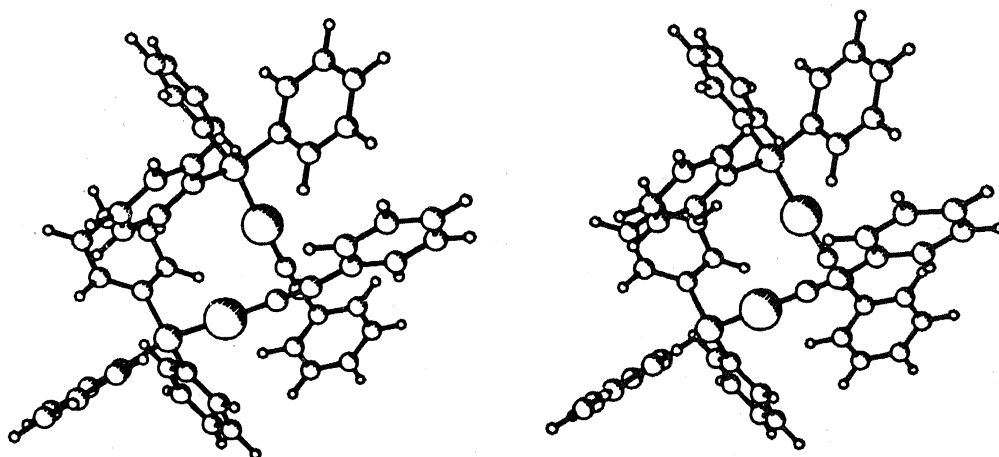


Figure 2. Stereoview of the crystal structure of (2-phenylethynyl) (triphenylphosphine) gold (I) (CSD refcode DUZYUS) to show the Au...Au interaction. Notice that the phenyl rings of the adjacent molecules dovetail via herringbone C...H interactions to give a dimeric structure. The Au...Au distance is 3.38 Å and the two non-equivalent torsion angles around the Au...Au contact are 74.3 and 104.3° (staggered geometry).

It is likely that the importance of these contacts will depend on the valency state of the metal and it is possible that similar interactions are important in Hg and U compounds.

3. Conclusions

Systematic studies of molecular inorganic crystals are in a nascent stage but several recent contributions hint at the richness of structural diversity that is contained in these compounds. Supramolecular assembly is well-exemplified by the use of the tetrahedral co-ordination of Cu(I) to generate double helical "DNA-like" structures (Dietrich-Buchecker and Sauvage 1989). Very elaborate yet precise electrostatic templating has been shown for a series of organometallic arene complexes (Fagan and Ward 1992). A unique blend of inorganic and organic structural chemistry is exhibited by the Cd thiolate clusters (Dance 1986). Extending this line of thought, the crystal structures of C_{60} and K_3C_{60} constitute a bridge between molecular and ionic solids. The use of the CSD to follow conformational deformations and, by implication, inorganic reaction pathways has been described (Orpen 1993). Many aspects of the crystal chemistry of Ru and Ir clusters have been discussed in detail (Braga 1992) and it has been shown that interactions such as C-H...O hydrogen bonding are important in some of these and related structures (Braga and Grepioni 1993; Onaka *et al* 1993). Main group element molecular solids have been far less studied. We have examined the phenomenon of halide ion hydration and have shown that the linearity of O-H...halide hydrogen bonding is the major factor which determines the geometry of these structures (Pathaneni and Desiraju 1993b).

In conclusion it should be emphasised that a study of the crystal rather than the molecular structures of molecular inorganic compounds offers much scope for a wider appreciation of supramolecular chemistry. Old and new compounds may be profitably studied. Regarding already determined crystal structures, the large amount of accurate crystallographic information now available in databases is an invaluable source of information. Such studies can extend the chemistry of these substances beyond the molecule to the supermolecule.

Acknowledgements

This paper reported some of the work done by Dr. S S Pathaneni during his tenure at the University of Hyderabad. Thanks are due to Professor P Pyykko, University of Helsinki, for making available unpublished material and to Mr D S Reddy for his assistance in the preparation of this manuscript.

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