

## Databases I-Small Molecule

**MS22.01.01 THE USE OF MULTIPLE DATABASES IN PRACTICAL MATERIALS IDENTIFICATION PROBLEMS.** James A. Kaduk, Amoco Corporation, P.O. Box 3011 MC F-9, Naperville IL 60566

The seven widely-available databases which contain crystallographic information - the Cambridge Structural Database, the Inorganic Crystal Structure Database, the Metals Data File, the Protein Data Bank, the Nucleic Acid Database, the Crystal Data Identification File, and the Powder Diffraction File - are powerful and cost-effective tools for solving materials identification problems. Just as no one analytical technique solves all problems, no one database yields all the desired answers. It is often necessary to use these databases in combination to solve a particular problem.

Examples of the combined use of the CSD, ICSD, CDIF, and PDF in solving practical problems will be discussed. The structures of several compounds - cobalt pyromellitate, magnesium ethoxide, the new borates  $K_2Al_2B_2O_7$  and  $SrAl_2B_2O_7$ ,  $Cu_2Al_6B_4O_{17}$ , a-PdCl<sub>2</sub>, and a-VO(PO<sub>3</sub>)<sub>2</sub> - will be described. To understand the true nature of each of these compounds, the use of multiple databases was required. The power of relational database technology applied to crystallographic databases will be illustrated briefly.

**MS22.01.02 COORDINATION OF LEAD (Pb) IN CRYSTAL STRUCTURES : A CAMBRIDGE STRUCTURAL DATABASE STUDY.** Liat Shimoni-Livny<sup>†</sup>, Charles W. Bock<sup>‡</sup>, Jenny P. Glusker<sup>†</sup>, The Institute for Cancer Research, Fox Chase Cancer Center, Philadelphia, Pennsylvania 19111, USA<sup>†</sup>. The Philadelphia College of Textiles and Science, Philadelphia, Pennsylvania 19144, USA<sup>‡</sup>

Lead is a member of the 'b'-class (soft) elements which, along with cadmium and tin, are potentially dangerous to humans. In its ionic state the plumbous ion Pb(II) is generally more stable than the plumbic ion Pb(IV).

This paper will describe the various modes of binding of lead in its different oxidation states as indicated by the results of crystal structure determination of small molecules solved to a high resolution along with *ab initio* molecular orbital calculations. We analyzed the preferred coordination numbers of lead, the chemical nature of the ligating atoms, and the geometry of its coordination sphere. Lead in the divalent state possesses, like germanium and tin, a lone pair of electrons in its outer shell. Divalent lead (Pb), with two electrons in its 6s orbital, due to its large atomic number (82) shows a relativistic effect<sup>1</sup> so that the inner shells contract and these 6s electrons are stabilized and may become an "inert pair." Thus the energy required to remove or interact with the 6s lone pair of electrons is increased, causing low symmetry around the lead ion. We examine here the geometrical and crystal packing consequences of the presence of this lone pair of electrons in the crystal structures of lead compounds found in the Cambridge Structural Database.<sup>2</sup>

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1. Pitzer, K.S. *Acc. Chem. Soc.*, **1979**, *12*, 271-276. Pyykko, P. and Desclaux, J.-P. *Acc. Chem. Soc.*, **1979**, *12*, 276-281. Pyykko, P. *Chem. Rev.*, **1988**, *88*, 563-594. McKeney, D. R. *J. Chem. Ed.*, **1983**, *60*, 112-116. Banna, M. S. *J. Chem. Ed.*, **1985**, *62*, 197-198.
2. Allen, F. H. et al. *Acta Crystallogr.* **1979**, *B35*, 2331-2339.

**MS22.01.03 STATISTICAL HYDROGEN BOND STUDIES BASED ON NEUTRON DIFFRACTION DATA.** Thomas Steiner, Institut für Kristallographie, Freie Universität Berlin, Takwtr. 6, D-14159 Berlin, Germany

Geometrical characterisation of X-H...Y hydrogen bonds requires knowledge of the H-atom position. Since this can be only qualitatively provided by X-ray diffraction, accurate hydrogen bond studies must be based on neutron diffraction data. Hydrogen bonds are soft interactions; therefore, the structural properties of hydrogen bonds cannot be deduced from individual crystal structures, but only from analysis and comparison of possibly large numbers of neutron diffraction studies. In this context, 'crystal correlation studies' using information extracted from crystallographic databases, in particular the CSD, have proven to be a powerful tool to gain insight into the nature of hydrogen bonding.

Only a number of examples can be presented that demonstrate the power of crystal correlation studies in this field:

- Directionality of X-H...Y hydrogen bonds, in particular the rapid decrease of directional behaviour with increasing H...Y separation. The importance of longrange H...Y interactions as components of multi-center hydrogen bonding.
- Lengthening of the X-H bond in X-H...Y interactions, which allusively even shows up for the weak C-H donors.

Some recent references: Th. Steiner & W. Saenger (1992). *Acta Cryst.* **B48**, 819.

Th. Steiner & W. Saenger (1994). *Acta Cryst.* **B50**, 348.

Th. Steiner, (1995) *J. Chem. Soc., Perkin Trans. 2*, 1315.

**MS22.01.04 A KNOWLEDGE BASE OF DERIVED INFORMATION FROM THE CAMBRIDGE STRUCTURAL DATABASE: NON-BONDED INTERACTIONS.** Jason C. Cole, Frank H. Allen, Jos P. M. Lommerse, R. Scott Rowland, Robin Taylor, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK

Databases provide users with easy access to a large amount of experimental data. Because of this, exploration of variations in experimental features as a result of different conditions is possible.

The Cambridge Structural Database (CSD) is an example of such a database. It has already been used to derive mean experimental bond lengths and angles for a large number of distinct chemical moieties. Such data is probably as important as the CSD itself and so also needs to be easily accessible to chemists in a so-called "knowledge base".

Because the CSD is a crystallographic database, it can be used to explore "non bonded" interactions as well as covalent interactions. We are currently developing a knowledge base of non-bonded interactions. It will convey information about both the types and directionality of non-bonded interactions for a wide selection of pharmaceutically interesting functional groups. The information will be presented as scatterplots and "vector" plots around the varying functional groups. These plots will be fully importable into molecular modelling packages (e.g. SYBYL). It is hoped that the information will assist in interactive ligand design. The data may also assist in parameterizing automated ligand docking programs.

The knowledge base will also contain theoretical results for some non-bonded interactions generated from Intermolecular Perturbation Theory (IMPT). This method is suited to calculations on molecular complexes since the energies produced are free of basis set superposition error.

In this talk, some of the generated data will be presented, along with an introduction to the menu-based system that will be utilised to access the data.