

MS29 O1

Combined Use of Structural Databases, Density Functional Calculations and Continuous Shape Measures: Application to Four-Coordinate Transition Metal Compounds [Santiago Alvarez](#), Jordi Cirera, Eliseo Ruiz. *Department de Química Inorgànica, Universitat de Barcelona, Barcelona, Spain.* E-mail: santiago@qi.ub.es

Keywords: Shape measures, DFT calculations, Structural databases

A DFT computational study combined with a structural shape analysis[1] of four-coordinate transition metal complexes covering all the d^n electron configurations ($0 \leq n \leq 10$). The results of such work allow us to present a renovated perspective of the stereochemical and spin state preferences in those families of compounds. In particular, our calculations confirm the predictions of a Walsh diagram on allowed and forbidden spin multiplicities of the ground state, as well as the choice of a different stereochemistry for each spin state, giving raise to the existence of *stereospinomers*, isomers that differ in both their spatial arrangement and spin state. [2] The importance of several factors in determining the preferred stereospinomer in each particular case will be evaluated, including the number of valence d electrons, the presence of π -donor ligands, the metal oxidation state, and the row of the periodic table to which the metal belongs, and some specific effects associated to the presence of ligands with different donor characteristics. The specific problem of the possible existence of low spin tetrahedral compounds can be predicted by means of a *magic cube* and the predictions are verified by comparison with a wide variety of structural data from the CSD and ICSD databases.

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[2] Cirera J., Ruiz E., Alvarez, S. *Chem. Eur. J.* 2006, 12, 3162.

MS29 O2

Crystal structures with $Z' > 1$ [Kirsty M. Anderson](#)^a, *Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK.* E-mail: k.m.anderson@durham.ac.uk

Keywords: Z' ; Crystal Packing, Crystal Engineering

The understanding and prediction of the crystal structures of solid state molecular compounds is of intense and increasing current interest. This interest is driven partly by increasing advances in technology and computing techniques leading to an unprecedented ability to study and control molecular solid state materials. Within this context the class of materials which crystallise with more than one molecule in the asymmetric unit (*i.e.* have $Z' > 1$) represent the most challenging frontier for understanding and predicting crystal structures. Around 8.8% of structures in the Cambridge Structural Database (CSD) crystallise with more than one molecule in the asymmetric unit (*i.e.* $Z' > 1$) with values ranging from $1 \frac{1}{12}$ to putatively 32. We have begun to rationalise some of the reasons behind the formation of structures with $Z' > 1$, for example we have shown that a resolved chiral species in combination with a compound containing a synthon with a strong predisposition to crystallise in a centrosymmetric

manner leads to structures with $Z' > 1$ more than 60% of the time. This and other systems with a tendency to form structures with high Z' values will be discussed, we will also show how we have used the knowledge gained to predict and synthesise further examples of structures with $Z' > 1$.



<http://www.durham.ac.uk/zprime>

[1] Anderson K. M.; Goeta A. E.; Hancock K. S. B.; Steed J. W.; *Chem. Commun.*, 2006, 2138 [2] Anderson K. M.; Afarinkia K.; Yu H.-W.; Goeta A. E.; Steed J. W. *Cryst. Growth Des.*, 2006, 6, 2109

MS29 O3

Analysis of Structural Relations in the CSD using IsoQuest2007: Clathrates of Cholic Acid and its Derivatives [René de Gelder](#), Jan M.M. Smits, *Molecular Materials, Institute for Molecules and Materials, Radboud University Nijmegen, The Netherlands.* E-mail: r.degelder@science.ru.nl

Keywords: isostructurality, structural classification, inclusion compounds

In the field of crystal engineering a correct classification of a set of structures can be essential for the understanding of the relation between physical properties and the underlying structures of materials. For understanding the phenomena of polymorphism and isostructurality methods are needed that objectively quantify the similarity of crystal structures. The IsoQuest program^{1,2} was developed for comparing sets of crystal structures and for exploring structural databases like the Cambridge Structural Database³ (CSD) for isostructurality and structural relations. IsoQuest tells you whether structures are identical or similar and results can be further analyzed with IsoBase, a database containing the complete analysis of all (50 billion) structural relations in the CSD on the basis of the IsoQuest principle.

We demonstrate the latest version of the IsoQuest program by analysing and classifying inclusion compounds of cholic acid and its derivatives. Cholic acid is one of the classical examples that forms inclusion compounds with an amazing number of solvents and other substances, and also its derivatives show remarkable cocrystallization capabilities. It is shown that IsoQuest2007 is a powerful tool for classifying related structures automatically, allowing for differences in chemistry, unit cell shape and volume and/or space group symmetry. Moreover, applied to structural databases it is a method to generate new information on packing principles and crystal engineering rules.

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