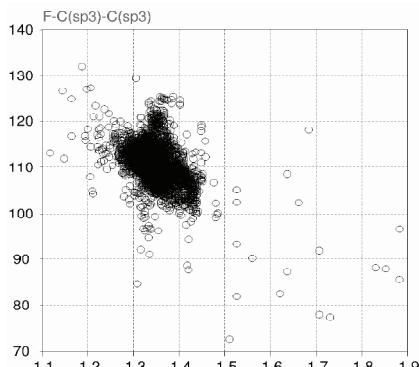


$R \leq 0.05$ . In spite of this restraints, the following scattergram shows that the dispersion of F-C distances and F-C-F angles is very broad, indicating that, in a large number of cases, disorder was possibly present but ignored by the authors. As a conclusion same typical cases of disorder will be discussed.



**Keywords:** weak interactions; analysis of disordered structures; fluorine compounds

#### FA4-MS10-P04

**Absolute Configuration Determination: Is There More Information in the Data?** David J. Watkin<sup>a</sup>, Amber L. Thompson<sup>a</sup>. <sup>a</sup>*Chemical Crystallography, Department of Inorganic Chemistry, Oxford.*

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A sample of unknown enantiopurity can be regarded as containing a mole fraction of a given hand equivalent to  $1-x$ , and  $x$  mole fraction of the other. Because the Flack  $x$  parameter [1] is a parameter in the refinement, its standard uncertainty  $u(x)$  can also be determined giving a measure of the confidence in the assignment of the absolute structure. Flack & Bernardinelli [2] give confidence intervals for the assignment of the absolute structure of materials of new samples: For a sample of unknown enantiopurity, the value of  $u(x)$  must be less than about 0.04 for  $x$  to be a reliable assignment of the chirality of the major component. If the material is known to be enantiopure, then the condition on  $u(x)$  can be relaxed to 0.10 and  $x$  in the range 0.3 to -0.3 would be considered as confirming the stated configuration.

Increasingly, there has been a suspicion that these conditions are over-cautious. By examining the distribution of the Friedel differences, Hooft et al. [3] have derived a parameter,  $y$ , which lies in the interval 0 to 1 and behaves something like the Flack  $x$  parameter. Because the calculation is working with distributions, there is the possibility of estimating the probability, for a known enantiopure material, that the assigned hand is correct. Hooft et al. remark, "These probabilities can be surprisingly decisive, even when the resonant scattering signal is very weak".

Examination of the Flack  $x$  and the Hooft  $y$  parameters for the natural product, epiallexine (below) raised some interesting questions [4]. In order to get a snap-shot of the performance of the Flack and Hooft parameters, 120 recent data sets collected on known enantiopure light atom

materials measured using molybdenum radiation [5] have been examined and results will be presented.

[1] Flack H.D. **1983**. *Acta Cryst.*, A39, 876-881. [2] Flack H.D. & Bernardinelli G. **2000**. *J. Appl. Cryst.*, 33, 1143-1148. [3] Hooft, R.W.W., Straver, L.H. & Spek A.L. **2008**. *J. Appl. Cryst.*, 41, 1, 96-103. [4] Thompson, A.L., Watkin, D.J., Gal, Z.A., Jones, L., Hollinshead, J., Jenkinson, S.F., Fleet G.W.F. & Nash R.J. **2008**. *Acta Cryst.*, C64, o649-o652. [5] Thompson A.L. & Watkin, D.J., *Tet. Asym.*, in press.

**Keywords:** absolute configuration determination; chirality; small-molecule crystallography

#### FA4-MS10-P05

**The Coordination Mode of the Carboxylate Ligands in Copper Complexes.** Goran A. Bogdanović<sup>a</sup>, Sldjana B. Novaković<sup>a</sup>. <sup>a</sup>*VINČA Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, P.O. Box 522, 11001 Belgrade, Serbia.*

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Oxygen atoms from the carboxylate group possess four free electron pairs what enables the formation of different coordination modes with different number of metal atoms. Over 5000 crystal structures of copper complexes with carboxylate ligands have been analyzed using the Cambridge Structural Database (CSD) [1]. We have performed the classification of Cu carboxylate complexes based on geometrical parameters and frequency of structural motifs related to different coordination modes. The majority of crystal structures extracted from CSD can be described by two structural motifs: a) the carboxylate group is a part of chelate ring (five- or six-membered) with one carboxyl oxygen coordinated to the Cu atom, b) the carboxylate group is a bridging ligand connecting two Cu atoms. The second group of crystal structures has been analyzed in more details using different geometrical parameters. We found some preferential Cu...Cu interatomic distances related to different coordination modes of the carboxylate group.

[1] Allen F.H., *Acta Crystallogr.*, **2002**, B58, 380.

**Keywords:** Cambridge structural database; chemistry of complex compounds; carboxylates

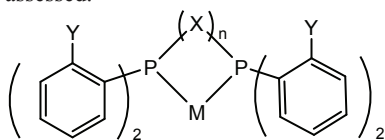
#### FA4-MS10-P06

**Conformational Analysis of Bidentate Tetra-Aryl Diphosphines.** Claire L. McMullin<sup>a</sup>, Natalie Fey<sup>a</sup>, A. Guy Orpen<sup>a</sup>. <sup>a</sup>*Department of Chemistry, University of Bristol, UK.*

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Phosphine ligands play an important role in many homogeneous catalytic reactions, including hydroformylation and asymmetric hydrogenation. In particular, bidentate tetra-aryl-substituted diphosphines allow fine-tuning of catalyst properties by modification

of ortho-substituents (Y) and chelate ring backbones ( $X_n$ ). These modifications can affect conformer preferences as well as potentially affording control (including stereo-control) of the reacting site. Conformations of these ligand types have been explored in new crystal structures and those in the Cambridge Structural Database[1]. These ligands have been assessed for possible chirality-inducing behavior using novel methods of quantification, and analysis of conformational preferences and the implications for the desymmetrisation of catalytically active complexes assessed.



**Fig. 1** – Bidentate tetra-aryl diphosphine chelating a metal (M), with varying backbone type and substitution.

[1] a. F.H. Allen, *Acta Cryst.*, **2002**, B58, 380-388. b. A.G. Orpen, *Acta Cryst.*, **2002**, B58, 398-406.

**Keywords:** catalysis; conformational analysis; crystal databases

#### FA4-MS10-P07

**New Structures of Old 2:1 and 3.1 ASN Salts to Quantify Fertilizers.** Santiago García-Granda<sup>a</sup>, Jose Montejo-Bernardo<sup>a</sup>. <sup>a</sup>*Department of Physical and Analytical Chemistry, University of Oviedo. Asturias, Spain.*

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*Ammonium Sulfate Nitrate* (ASN) fertilizer is one of the first synthetic fertilizers, and has been used for nearly the last 100 years. It is mainly a combination of the double salts 2AN:AS and 3AN:AS (AN ammonium nitrate; AS ammonium sulfate).

It is a source of primary (nitrogen) and secondary (sulfur) nutrients. Due to the soil needs and security (it is explosive), the commercial ASN fertilizer ought to contain 26% nitrogen and 13-14% sulfur. This quantification is complicated and has to be done by indirect measures (i.e. by the percentages of the oxides). Even though the existence of these double salts is known since a century ago [1], their structures *have* not been reported and are absent of the crystallographic data bases. The scarce work of quantification using X-ray diffraction data was done using the RIR method [2]. In our work [3] the crystal structures of both double salts, solved by X-ray single crystal data, are reported both at room and low (100 K) temperatures. The results of the quantification of several industrial samples of ASN fertilizers by Rietveld fitting using these structural data are presented and discussed.

[1] Schreinemakers F.A.H., Hoenen P.H.J., *Chemisch Weekblad*, **1909**, 6, 51-56. [2] Highsmith R.E., Kweeder J.A., Correal S.T., *US Patent 2002/0095966A1*, **2002**. [3] Montejo-Bernardo J.M., García-Granda S. Submitted to *Acta Cryst. B*.

**Keywords:** fertilizer; rietveld quantification; databases

#### FA4-MS10-P08

**Group-Subgroup Relationships For Metal-Dioxide Phases: From Hettotypes up to Archetypes.** Yury E. Kitaev<sup>a,b</sup>, Mois I.Aroyo<sup>a</sup>, Andrey G.Panfilov<sup>a,b</sup>.

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Metal dioxides ( $MeO_2$ ,  $Me = Zr, Hf, Sn, Pb, Ti, Te, etc.$ ) exhibit many common phases (fluorite, rutile, baddeleyite, cottunite, etc) and even similar sequences of phase transitions at the pressure-temperature phase diagram [1]. Using the Retrieval Tools from the Bilbao Crystallographic Server [2], [3] we construct the group-subgroup relationship tree, also known as the Bärnighausen tree, which allows us to reveal common features of these compounds as well as to predict some intermediate phases. We propose constructing the Bärnighausen trees beginning with the lowest hettotypes up to the highest possible aristotypes. The procedure can be described as follows: i) beginning with hettotypes we found their minimal supergroups; ii) we select only those supergroups whose Wyckoff positions split into the occupied positions of the hettotypes; iii) the procedure continues up to the highest symmetry structure which has no supergroup: we call it the *archetype* of a given crystal family. In this procedure, the archetypes are obtained as a result of the construction procedure whereas when constructing the tree beginning with the aristotype, the choice of the latter is ambiguous: there could be several high-symmetry phases which are not connected by group-subgroup relationships. In the proposed procedure, these phases will be included into the tree as belonging to different branches. The tree branches lead to archetypes. Next, when constructing the tree beginning with aristotypes, the number of paths is very large since all maximal subgroups of the aristotype are allowed. The path selection is made by comparison with the observed phases. In our procedure, the choice of paths is based on the Wyckoff position splitting scheme, only. In general, a crystal family can have several archetypes. The archetypes appear to be the close-packed structures. The analysis shows that for the  $MeO_2$  crystal family, the Bärnighausen tree has the *fcc* close-packed fluorite-type structure as a single archetype. Nineteen dioxides  $MeO_2$  ( $Me = Rb, Zr, Hf, Sn, Pb, Po, Si, Ce, Pr, Tb, Th, Pa, U, Np, Pu, Am, Bk, Cf, Te$ ) have been observed with the fluorite-type structure. For other compounds, like  $TiO_2$ , the fluorite structure is proposed as a possible high-temperature and/or high-pressure phase. We also suggest symmetry assignments to the observed  $C^*$ , ORTH-III, and ORTH-V phases for the  $ZrO_2$  crystal. We acknowledge the support of IKERBASQUE Basque Foundation for Science.

[1] Merril L. *J. Phys. Chem. Ref. Data* **2005**, 11, 1005. [2] Aroyo M.I., Perez-Mato J.M., Capillas C., Kroumova E., Ivantchev S., Madariaga G., Kirov A., Wondratschek H., *Z.Kristallgr.* **2006**, 221, 15. [3] Bilbao Crystallographic Server [www.cryst.ehu.es](http://www.cryst.ehu.es)

**Keywords:** group-subgroup relations; metal oxide, bilbao crystallographic server