

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.

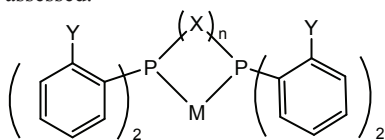


Fig. 1 – Bidentate tetra-aryl diphosphine chelating a metal (M), with varying backbone type and substitution.

[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^a, Jose Montejo-Bernardo^a. ^a*Department of Physical and Analytical Chemistry, University of Oviedo, Asturias, Spain.*

E-mail: sgg@uniovi.es

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^{a,b}, Mois I.Aroyo^a, Andrey G.Panfilov^{a,b}.

^a*Departamento de Física de la Materia Condensada, Universidad del País Vasco, Bilbao, Spain.* ^b*Ioffe Physical-Technical Institute, St-Petersburg, Russia.*

E-mail: kitaev@wm.lc.ehu.es

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

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