

Engineering Inorganic Crystals

PS08.03.01 CONSIDERATION OF BRIDGING GEOMETRIES IN RATIONAL SYNTHESIS OF OXOVANADIUM PHOSPHATES. Marcus R. Bond and Tom Otieno, Departments of Chemistry, Southeast Missouri State University, Cape Girardeau, MO 63701 and Eastern Kentucky University, Richmond, KY 40475

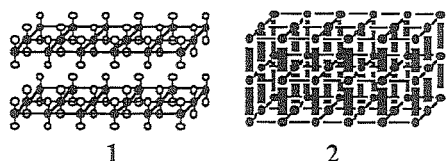
While the preparation of new oxovanadium phosphate structural frameworks still lies largely in the realm of serendipity, the significant accumulation of structural data for these systems provides a foundation for developing rational synthetic strategies. The diversity of bridge types found in oxovanadium phosphates undoubtedly leads to the complicated array of observed structural types. Within these systems both one-atom ($\mu\text{-O}$) and three-atom ($\mu\text{-O}$, $\mu\text{-O}'$) bridges are found in single, double, triple, or quadruple bridges between oxovanadium centers. Double three-atom bridges provide the most variety offering at least seven distinct bridge configurations each with a wide range of distorted conformers. Systematic analysis of known bridge types, their geometries, and structural environments provides insight into the factors that govern adoption of various bridging modes and geometries in oxovanadium phosphate clusters and extended solids.

PS08.03.02 FINDING COMPOUND PROPERTY PATTERNS IN EMPIRICAL DATA SETS USING DISCOVERY METHODS. A. G. Jackson, Wright Laboratory, WPAFB, OH, USA, N. Kiselyova, Baikov Institute of Metallurgy, Moscow, Russia.

Extension of performance of materials beyond the current limits for bulk or thin films has become imperative because of demands for high performance. Frequently this means new materials must be designed that build on existing compounds in ways not easily determined using first principles computational approaches. Methods for exploring data bases to identify patterns of behavior are useful because of the classification and prediction possibilities they offer. The pyramidal net method has been applied to the prediction of new compounds based on known data on the elements of the compounds. Compound types A_3BC_{15} , ABF_5 , ABF_6 , ABO_3 have been considered using several forms of feature sets that include a number of properties of the elements and of archetype compounds where known. A Table of predicted compounds resulted from the analysis.

PS08.03.03 MOLECULAR CHAINS, GRIDS AND CUBICLES: DESIGNING INORGANIC POROUS SOLIDS. Pierre Losier, Donald C. MacQuarrie and Michael J. Zaworotko, Department of Chemistry, Saint Marys University, Halifax, Nova Scotia, B3H 3C3 Canada.

Crystal engineering has led to the rational design of inorganic polymers containing one- (chains), two- (grids), and three-dimensional (boxes or cubicles) frameworks based upon the established coordination chemistry of the incorporated transition metals (e.g. Co, Ni, Cu, Cd, Zn). Few solids consisting of square planar grids (1) have been reported and the large cavities in these two-dimensional frameworks (>50% by volume) usually lead to interpenetration or enmeshing of one grid into another which results in a reduction or elimination of effective pore size. Recently, we reported the synthesis and structural characterization of an octahedral porous solid (2), $[\text{Zn}(4,4'\text{-dipyridyl})_2]\text{SiF}_6 \cdot x \text{DMF}$, which consists of overlapping grids of $[\text{Zn}(4,4'\text{-dipyridyl})_2]$ linked by the counterion $[\text{SiF}_6]^{2-}$. This neutral inorganic polymer eschews interpenetration and has its cavities filled with solvent molecules. We present herein several examples of non-interpenetrated square grid and octahedral inorganic polymers.



● metal — linear 'spacer' ○ loosely held anion or ligand ■ bifunctional anion

Systematics of Organics and Analysis

PS08.04.01 IN THE MEMORY OF LINUS PAULING. PARSIMONY. N. L. Smirnova, Moscow State University, Geological Department, Vorobyevy Gory, 119899, Moscow, Russia

Parsimony is one of the universal laws of nature. L. Pauling published five well known rules by him in 1929. He gave the name "parsimony" to the fifth rule which reads: the number of essentially different kinds of constituents in the crystal tends to be small. The attitude of scientists towards this rule is different: some of them decline it (N. V. Belov, V. S. Urusov, 1991), some ignore it (F. Libau, 1988, F. Wells, 1987, L. Pauling in his later publications), some refer to it without comments (B.F. Ormont, 1950, T. Penkal, 1974) some consider it to be less universal than four remaining rules (J. B. Boky, 1971), some apply it to intermetallic structures (F. Laves, 1939), some use it to simulate the structure of inorganic compounds (N. L. Smirnova, 1952 and later publications, V. S. Urusov, L. A. Dubrovinskaya, L. S. Dubrovinsky, 1990) some consider it as an universal law, small numbers being ranged from 1 to 4 (N. L. Smirnova, 1971); in case of a strict parsimony the ancestor should be determined, in case of mild parsimony - members of series (N. L. Smirnova, 1952, 1956 etc.) a more precise definition reads: the number of essentially different kinds of substituents (at least for one of them tends to be small (N. L. Smirnova, 1993). The rule suggests an estimation using four qualitative characteristics, as well as the largest frequency of 1-4-ary combinations. The parsimony rule has been established for formulas of different kinds: positional formulas for structural types and classes, for *sfdp* formulas (N. L. Smirnova, 1993, 1994) for types of the atomic environment (J. L. C. Daams, P. V. Villars), for properties (N. L. Smirnova, 1995, 1996).

Exotic Molecules-Inorganic/Mineral

PS08.05.01 CRYSTAL STRUCTURES OF NEW DOUBLE HYDROGEN PHOSPHATES WITH ENORMOUS UNIT CELLS. N. Anisimova, A. Ilyukhin, and N. Chudinova, Institute of General and Inorganic Chemistry, Russian Academy of Science, Moscow 117907, Russia

Recently published [1] the direct method for the synthesis of cyclododecaphosphates (the biggest inorganic phosphate ring) includes the consistent thermal condensation of double cesium iron hydrogen monophosphate into cyclododecaphosphate $\text{Cs}_3\text{Fe}_3\text{P}_{12}\text{O}_{36}$. In the work [1] the previously unknown substance $\text{CsFeH}_5(\text{PO}_4)_3$ was firstly obtained and used as a starting material. The present work reports its crystal structure as well as the previously unknown structure of $\text{NaFe}(\text{H}_2\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$. Unit cells of both compounds are characterized by the large dimensions unusual for other known inorganic hydrogen phosphates. The main structural elements of the structures of $\text{CsFeH}_5(\text{PO}_4)_3$ ($R=0,029$; Pna_21 , $Z=12$; $a=27.18(1)$, $b=9.081(3)$, $c=12.808(4)$ Å) and of $\text{NaFe}(\text{H}_2\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ ($R=0,036$; $Pbcn$, $Z=8$; $a=8.7291(7)$, $b=12.4954(8)$, $c=18.944(1)$ Å) are the channels formed by PO_4 -tetrahedra and FeO_6 -octahedra. Cs and Na atoms are placed inside the channels. Due to their specific structures both compounds are essential for the formation of new complex phosphate anions.

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[1] U. Skütülke, N. Anisimova, and P. Neumann, *Z. anorg. allg. chem.*, 1996, in print.