

m39.p08

Packing behaviour in pseudo Vaska-type complexes

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Keywords: rhodium, disorder, platinum group

Pseudo Vaska-type complexes, *trans*-[M(X)(Y)(ZR₃)₂] (M=Rh, Ir if X=CO, NCS, NCO and M=Pt, Pd if X=Cl, Me; Y=halogen, Z=Group 15 atom, R=aryl, alkyl) can undergo various key step catalytic reactions, e.g. oxidative addition, reductive elimination, substitution, insertion, etc., manifesting them as well-behaved model complexes for various catalytic systems [1]. These complexes are easy to synthesize and can be investigated structurally due to their favorable thermal stability. Data obtained from solid-state investigations can then be correlated with solution IR and ³¹P NMR spectroscopy for the CO and PR₃ ligands to evaluate different ligand effects. However, these complexes are also well known for their tendency to be statistically disordered along the X-M-Y axis, thus decreasing accuracy of the solid-state data in some cases, leading to incorrect correlations. Complexes to be discussed in this presentation form part of a study to determine which factors govern the packing disorder [2].

[1] A. Roodt, S. Otto and G. Steyl, *Coord. Chem. Revs.* 2003, 245, 121-137. [2] For examples, see: (a) R. Meijboom, A. Muller, A. Roodt, J. M. Janse van Rensburg, *Acta Cryst.* 2006, E62, m894.

[2] R. Meijboom, A. Muller, A. Roodt, *Acta Cryst.* 2006, E62, m682; (c) R. Meijboom, A. Muller, A. Roodt, *Acta Cryst.* 2006, E62, m1309.

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Mild Hydrothermal Synthesis and Structural Study of a New Nickel Pyrazine Vanadate

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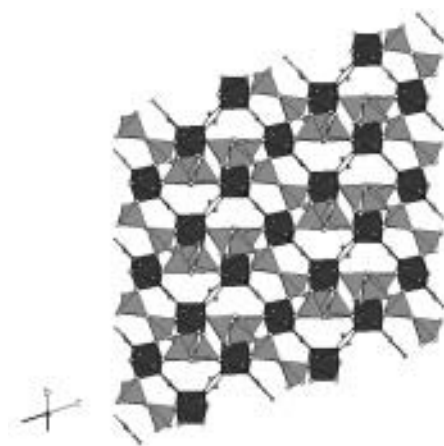
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Keywords: vanadates, hydrothermal synthesis, inorganic and organic crystal structures

The chemistry of the polioxovanadate/metal-organic ligand compounds is very rich due to the great ability of vanadium to adopt different coordination environments and oxidation states. This has allowed to obtain in the last years, a great variety of structures with polioxovanadates forming clusters, chains and three-dimensional networks^[1]. This way a new polioxovanadate of nickel with pyrazine has been synthesized.

The Ni_{1.5}V₄O_{11.5}(C₄H₄N₂)_{1.5} was obtained by mild hydrothermal synthesis of a mixture of Ni(NO₃)₂·6H₂O, NaVO₃, pyrazine and water. The compound crystallizes in the P-1 triclinic space group, with a = 8.556(2) Å, b = 9.117(2) Å, c = 12.619(3) Å, α = 71.05(2)°, β = 83.48(2)°, γ = 61.32(3)° and Z = 2. X-ray diffraction data were collected on an Oxford Diffraction XCALIBUR2 automatic diffractometer. The structure was solved by direct methods (SHELXS97^[2]) and all non-hydrogen atoms were refined anisotropically. At convergence, R₁ = 0.0272 and wR₂ = 0.0439.

The structure of Ni_{1.5}V₄O_{11.5}(C₄H₄N₂)_{1.5} is built up from VO₄ tetrahedra and NiO₄N₂ octahedra. The corner-sharing VO₄ units form 12-members rings fused along the [1 0 0] direction. There are two types of nickel octahedra, Ni(1)O₄N₂ which have the pyrazine ligands in *trans*, and the Ni(2)O₄N₂, which have the pyrazine ligands in *cis*. The NiO₄N₂ octahedra are linked across the molecules of pyrazine forming zig-zag chains. These chains of [NiO₄(C₄H₄N₂)₂]_n are linked to the VO₄ tetrahedra *via* vertex belonging to the NiO₄N₂ octahedra, forming a three-dimensional network.



Acknowledgements: E. Serrano wishes to thank the UPV/EHU for funding.

[1] Hagrman, P.J., Finn, R.C., Zubieta, J., *Solid State Sciences*, 2001, 3, 745.

[2] Sheldrick, G.M., SHELXS97: *Program for the solution of crystal structures*, University of Göttingen, Germany, 1997.