PS02.05.14 CRYSTAL STRUCTURE DETERMINATION OF TWO POLYMORPHIC PHASES OF LANTHANUM NITRATE TETRAHYDRATE FROM X-RAY POWDER DIFFRACTION.

Two polymorphic varieties of La(NO₃)₃·4H₂O have been identified from temperature dependent X-ray diffraction experiments of the hexahydrate carried out in different water pressures. The two phases α and β are obtained for P(H₂O) greater and lower than 4 Torr, respectively. Powder diffraction data for the two phases were collected with a high resolution powder diffractometer using monochromatic radiation (λ = 1.5406 Å). The indexing of the powder patterns was performed by the successive dichotomy method (DICVOL91), the structure solutions were obtained from Patterson maps and subsequent Fourier analyses and, finally, the models were refined by the Rietveld method (FULLPROF).

ψ-La(NO₃)₃·4H₂O. P2₁/m. a = 6.778(1), b = 11.834(1) Å, c = 12.973(1) Å, V = 2027.3 Å³, Z = 8, Mₙ0 = 60, Fₚ = 85(0.0048, 74). The Rietveld refinement (71 varying parameters) converged to Rwp = 0.05 and R₁ = 0.08. The structure consists of infinite chains, formed by 11-coordinated La atoms, running along [001]. The polyhedra, formed by three bidentate, one monodentate nitrate groups and four water molecules, are connected through a bridging nitrate group. The cohesion of the structure is ensured by a network of hydrogen bonds. The 11-coordination of lanthanum has also been reported for the structure of the hexahydrate precursor. β-La(NO₃)₃·4H₂O. Pbcn, a = 13.531(1), b = 11.834(1) Å, c = 12.973(1) Å, V = 2027.3 Å³, Z = 8, Mₙ0 = 60, Fₚ = 85(0.0048, 74). The Rietveld refinement (71 varying parameters) converged to Rwp = 0.06 and R₁ = 0.12. The structure consists of infinite chains, formed by 10-coordinated La atoms, running along [001]. The polyhedra are formed by two bidentate, two bridging monodentate nitrate groups and four water molecules.

PS02.05.15 AB INITIO CRYSTAL STRUCTURE DETERMINATION FROM LOW TEMPERATURE X-RAY POWDER DATA: THE CHIRAL COMPLEX I-CARVONE-C₅H₅NO₂.
C. Miravitlles*, J. Ripoll, J. Sureau, M. A. Cuevas & T. Calvet(* Instituto de Ciencia de Materiales de Barcelona, c/nsp., UAB, 08193 Bellaterra, Spain) (fac. de Geologia, Univ. de Barcelona, c/ Maristres 2, Barcelona, Spain.

The ab initio structure determination of the chiral complex I-carvone (C₅H₅NO₂) at 218 K is presented. The pattern was measured with CuKα radiation, a position sensitive detector and the sample, liquid at room temperature, included in a glass capillary. The crystal data are: orthorhombic P2₁2₁2₁ with a = 6.8576(3) Å, b = 6.8851(5) Å, c = 19.9864(2) Å, Z = 4. The structure was solved by Patterson method using the 44 available integrated intensities. A rigid-body Rietveld refinement with preferred orientation correction and allowing the variation of one torsion angle converged to Rwp = 0.03 and Rwp = 0.04.

Perspective view of the I-carvone crystal structure at 218 K.

PS02.05.16 CRYSTAL STRUCTURE OF A NEW COORDINATION POLYMER, [(Ni₂Cl₂(L)(CH₂OH)₃(H₂O)]Cl₂·6H₂O, FROM X-RAY POWDER DATA.
A. Neels, B. Mathieu Neels and H. Stoeckli-Evans.

Coordination metal complexes with polymeric structures are of special interest in the development of new materials. Molecular ferromagnets and non-linear optical materials are the most important applications of such coordination polymers. 2,5-Bis(2-pyridyl)pyrazine (L) has been used as molecular bridge between metal centers. Some binuclear complexes and a two-dimensional polymer with 3d transition metals are characterized by their single-crystal X-ray structure [1].

Crystal structure of the title compound was obtained in micro-crystalline form. The structure was determined ab initio from X-ray powder diffraction data. The compound belong to the triclinic space group P1 with a = 8.7014(4) Å, b = 10.1465(5) Å, c = 8.0303(3) Å, α = 116.095(2)°, β = 112.713(3)°, γ = 74.0563(5)°. The final agreement factors are Rwp = 0.124, Rf = 0.095, and Rp = 0.045.

The octahedral coordination of the nickel atom is achieved by two nitrogens of the ligand 2,5-bis(2-pyridyl)pyrazine, two chlorines and two oxygens of the coordinated solvent molecules. The bridging nature of chloride ions and bis-bidentate ligands (L) leads to a one-dimensional polymer.


PS02.05.17 AlMethylPO₄·H₂O: THE AB INITIO STRUCTURE SOLUTION OF A NEW LAYERED COMPOUND.

Micro-porous and layered aluminosilicate mordenites offer wide-ranged possibilities in separation and catalysis. The title compound is a novel structure made up of aluminophosphate layers containing bound water, the layers being separated by methyl groups. The synthesis and structure solution of AlMethylPO₄·H₂O is described. The structure was solved ab initio from laboratory X-ray data using a combination of Direct Methods, molecular modeling and Rietveld refinement. Indexing gave a monoclinic unit cell of: a = 9.445 Å, b = 7.06 Å, c = 7.85 Å and β = 106.6° in the space group P2₁/a. A default run of the Direct Methods package SIRPLOW gave a starting structure consisting of 1P, 1A1 and 30’s. The remaining atoms were found through the use of difference Fourier maps and the Biosym modeling package, Insight. Which, combined with a prior knowledge of bond angles and distances for both octahedral and tetrahedral aluminium sites was used in the latter stages of the Rietveld refinement to determine starting positions for 5P’s and 5H’s. The result was a final structure solution with an Rwp of 7.85%, an Rp of 5.87% and a chi² of 5.39%.