

emerging nascent chain, binds to the large ribosomal subunit in the vicinity of the tunnel opening and forms a sheltered folding space. The 3.5 Å crystal structure of the large ribosomal subunit of the eubacterium *Deinococcus radiodurans*, D50S, in complex with the TF binding domain (TFa) from *Deinococcus radiodurans*, reveals for the first time the molecular structure of the entire TFa bound to the bacterial ribosome. In comparison with structures of isolated TF/TFa molecules from different bacterial sources, the current structure displays a conformational change in the TFa domain that assures a degree of dynamic flexibility and may hint at mobility during early folding.

The signature part of TFa anchors on small exposed regions of ribosomal proteins L23 and L29 some 40 Å away from the opening of the exit tunnel, in general agreement with the reported chimeric structure of the archaeal large ribosomal subunit (H50S) with the eubacterial TFa (Ferbitz et al., 2004). The chaperone TF does not exist in the archaeal kingdom, and therefore the similarity of its local interactions with both ribosomal systems highlights the high structural and sequence conservation of its contact region on the ribosome. Still, the archaeal ribosomal protein L23 lacks the sizable elongated loop, present in bacteria, which extends into the tunnel opening and can actively interact with the nascent protein passing through it. Our structure shows that TFa binds to two separate regions of L23 on both sides of the extended loop, thus linking the TF binding site with the ribosomal tunnel and enabling communication with the newly synthesized nascent chain.

Keywords: ribosome, chaperone, ribosomal tunnel

MS79 INORGANIC AND MINERAL STRUCTURES SOLVED AND REFINED BY POWDER DIFFRACTION DATA

Chairpersons: Jordi Rius, Evgeny Antipov

MS79.29.1

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NMR and PXRD Analysis of the Structure of a New Hydrous Layer Silicate

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RUB-39 is a synthetic hydrous layer silicate with an unusual crystal structure. Upon heating neighboring layers condense to a framework silicate with empty zeolitic pores. The crystal structure RUB-39 (P 2/c, $a = 7.3312(1)$ Å, $b = 10.7238(1)$ Å, $c = 17.5135(1)$ Å, $\beta = 115.6911(6)^\circ$) was solved from PXRD data and refined in its hydrated layered form with FULLPROF to final $\chi^2 = 3.1$. The diffraction analysis also allowed for a detailed analysis of the organic species used as structure directing agent (SDA) which is intercalated between silicate layers.

¹H solid state NMR experiments were used to study the role of the intercalated water and SDA-cation. The low field signal at 16.7 ppm indicates a strong hydrogen bond which is connecting neighboring silicate layers. This is unusual and might explain the topotactic condensation reaction upon heating. The spectrum also reveals that molecular water in intercalated in the interlayer space which is released only at temperatures above 170 °C.

PXRD and NMR studies following the further heating of the material to temperatures above 250 °C showed the breakdown of the SDA and the condensation process of the silicate. Attempts to isolate the SDA-free layered material failed so far since concomitant to the release of the intercalated molecules the condensation to the framework silicate sets in.

Keywords: powder XRD, solid state NMR, hydrous layer silicate

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Adventures in Solving Structures of Inorganic Compounds Using Powder Diffraction Data

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Anhydrous hygroscopic Pd(NO₃)₂ can be prepared by evaporating a commercial palladium nitrate solution to dryness in a vacuum oven at 50–60 °C. It crystallizes in space group $P2_1/a$, with $a = 10.0886(10)$, $b = 5.395(6)$, $c = 5.7484(5)$ Å, $\beta = 97.377(7)^\circ$, $V = 310.28(5)$ Å³, and $Z = 2$. The Pd was placed at the origin, and the N and O atoms located by difference Fourier techniques. The structure consists of discrete planar Pd(NO₃)₂ molecules. The molecular solid is an insulator with a bandgap of ~2.3 eV.

An attempt to prepare a magnesium vanadate using hydrothermal techniques yielded a hygroscopic new compound. The pattern could be indexed in space group $Cmcm$ with $a = 6.3727(7)$, $b = 13.5715(8)$, $c = 6.3657(4)$ Å, and $V = 550.56(8)$ Å³. The structure was solved by direct methods and difference Fourier techniques. The Rietveld refinement clearly indicated that the compound (Mg_{0.37}V_{0.63})O_{0.63}(SO₄)(H₂O)_{1.5} has a layered structure.

The powder pattern of the potential thermoelectric material NaGe₄ could be indexed on a primitive hexagonal cell. The structure was solved and refined in $P6/m$ with $a = 15.05399(5)$, $c = 3.96845(2)$ Å, and $V = 778.852(4)$ Å³. It consists of a zeolite-like Ge framework, with partially-occupied sites in a large 24-ring channel. Progress on the crystal structure of the mineral charoite, K(Ca,Na)₂Si₄O₁₀(OH,F)(H₂O), will also be discussed.

Keywords: palladium nitrate, vanadium sulfate hydrate, sodium germanium

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New Cathodes for Solid Oxide Fuel Cells studied by Powder

Diffraction: the System (A1-xA'x)FeO3

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A new family of iron oxide perovskites A_{1-x}A'_xFeO₃ (A = Nd, Pr, La; A' = Ca, Sr) has been studied for its potential use as cathodes in solid oxide fuel cells (SOFC). This is part of a collaboration between Basque Country University and Ikerlan Technological Research Centre (MCC Group) towards the development of metal supported intermediate temperature SOFC. Samples with a systematic change in doping level were prepared by the ceramic and combustion methods and characterised by laboratory X-ray powder diffraction and SEM. Electrochemical measurements were performed in the 600–850 °C temperature range on bulk and as electrodes in YSZ supported half-cells. A summary of these results will be presented in this work.

K. Vidal, thanks the Gobierno Vasco/Eusko Jaularitzta for a doctoral fellowship.

Keywords: crystal structure determination X-ray powder data, perovskite structures, conductivity

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Crystal Structure of the Superconducting Layered Cobaltate Na_xCoO₂yD₂O

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Superconductivity in layered Na_xCoO₂yH₂O occurs in CoO₂ sheets that have a quasi 2D triangular symmetry, analogous to that of geometrically frustrated systems. This is in stark contrast to the well know perovskite high-T_c cuprates, and makes the determination of the structural details of this novel superconductor essential in the understanding of its properties. However, due to the complexity of the intercalation of the H₂O between Na and CoO₂ sheets, details of the crystal structure of these materials have remained ambiguous. We have used electron and neutron powder diffraction to elucidate the structural properties of superconducting Na_xCoO₂yD₂O over a wide compositional range. Our measurements show that superconducting samples exhibit a number of supercells ranging from 1/3a* to 1/15a*,

but the predominant modulation, observed also in the neutron data, is a double hexagonal cell with dimensions $2a \times 2a \times c$. Rietveld analysis reveals that D_2O is inserted between CoO_2 sheets as to form a layered network of NaO_6 triangular prisms. Our model removes the need to invoke a 5K superconducting point compound and suggests that a solid solution of Na is possible within a constant amount of water y.

Keywords: oxide superconductors, powder neutron diffraction, bound water

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Structural Studies of the $A_3CoNb_2O_9$ "1:2" Ordered Perovskites ($A = Ca^{2+}, Sr^{2+}, Ba^{2+}$)

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A TEM, XRD and bond valence sum study of the $A_3CoNb_2O_9$ ($A = Ca^{2+}, Sr^{2+}, Ba^{2+}$) "1:2" perovskite compounds found $P-3m1$ ($\mathbf{a} = \mathbf{b}_p - \mathbf{c}_p$, $\mathbf{b} = -\mathbf{a}_p + \mathbf{c}_p$, $\mathbf{c} = \mathbf{a}_p + \mathbf{b}_p + \mathbf{c}_p$) symmetry for the $A = Ba$ compound and $P12_1/c1$ ($\mathbf{a} = \mathbf{a}_p + \mathbf{b}_p + 2\mathbf{c}_p$, $\mathbf{b} = \mathbf{a}_p - \mathbf{b}_p$, $\mathbf{c} = 3(\mathbf{a}_p + \mathbf{b}_p)$, subscript p for the perovskite parent sub-structure) symmetry for the $A = Sr$ and Ca compounds. All three compounds exhibit B -site Co/Nb ordering in layers along a $[111]_p$ direction. The Sr and Ca compounds exhibit octahedral tilting as well as minor octahedral distortion. A constrained modulation wave approach to Rietveld refinement of neutron powder diffraction data was used to determine their crystal structures.

$Ba_3CoNb_2O_9$ exhibited fine scale twinning and translational stacking faulting (apparent in HREM images and in powder diffraction data as systematic discrepancies between predicted and observed intensities of satellite reflections). The effect of such stacking faulting was modelled by refining the amount of two stacking faulted variants (offset by displacive shifts of $\pm \mathbf{R}$) in addition to the main variant.

The Sr and Ca compounds, each with 42 refinable atomic fractional coordinates, showed rather less fine scale faulting and refined normally - these being amongst the first reported successful neutron powder refinements of tilted 1:2 perovskites.

Keywords: perovskite oxides, structural characterisation, neutron diffraction

MS80 STRUCTURAL KNOWLEDGE AND CATALYSIS

Chairpersons: Jean-Claude Daran, Pilar Gómez-Sal

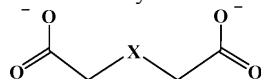
MS80.29.1

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Structural Diversity and Properties of Oxydiacetate and Thiodiacetate Mn Complexes

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In this communication we will present the results obtained in the area of oxydiacetate (oda) and thiodiacetate (tda) compounds of manganese. In particular, we will describe the synthesis and characterization of the aquo-complexes $[Mn(oda)(H_2O)]_n$ and $[Mn(tda)(H_2O)]_n$, and their reactivity versus N-donor ligands [1,2].



X = O, oda; S, tda

For example, we highlight the formation of compound $[Mn(tda)(bipy)]_n$, which is the first fully documented example of a tetracarboxylate dimanganese species containing a copper-acetate like core [2]. Furthermore, the comparison of the structures of the latter complex and those of related compounds with some substituted bipy ligands allow us to conclude that the geometry of the building block in $[Mn(tda)(bipy)]_n$ is imposed by the non-covalent interactions between the coordination polymers in the whole supramolecular structure. Finally, we will communicate some results concerning the use of these compounds as catalysts precursors in some model oxidation reactions.

[1] Grirrane A., Pastor A., Álvarez E., Mealli C., Ienco A., Rosa P., Montilla F., Galindo A., *Eur. J. Inorg. Chem.*, 2004, 707. [2] Grirrane A., Pastor A., Galindo A., Ienco A., Mealli C., *Chem. Commun.*, 2003, 512.

Keywords: manganese, oxydation, crystal structures

MS80.29.2

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Structure and Sense of Enantioselection of Rhodium Complexes of P-Chiral Diphosphines

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Optically pure P-chiral diphosphine ligands (1,2-bis((*o*-alkylphenyl)phenylphosphino)ethanes, 1,2-bis(alkylmethylphosphino)ethanes (BisP*), bis(alkylmethylphosphino)methane (MiniPHOS), and related ligands) were prepared via phosphine-boranes as the intermediates. The rhodium complexes of these ligands were used for the asymmetric hydrogenation of dehydroamino acid derivatives including beta-disubstituted derivative and beta-(acylamino)acrylates. Markedly high to almost perfect enantioselectivity was observed in these hydrogenations. The molecular structures of these complexes were determined by single crystal X-ray analysis. In the BisP* and MiniPHOS series, the bulky alkyl groups effectively shield the two diagonal quadrants and the methyl groups are placed at the other quadrants. The excellent enantioselection is responsible for this imposed asymmetric environment. Mechanistic study by multinuclear NMR indicates that the dihydride mechanism is operating in these hydrogenations and the enantioselection is determined at the migratory insertion step. The exact relationship between the sense of enantioselection and the molecular structure of the catalysts is presented.

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Keywords: asymmetric catalysis, chiral recognition, rhodium compounds

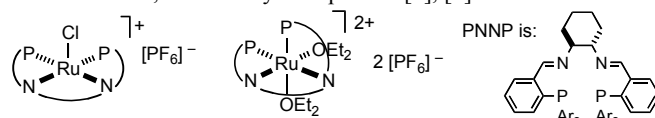
MS80.29.3

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Understanding Stereoselective Atom-transfer Reactions of Chiral Ruthenium Complexes

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In an atom-transfer reaction, a group or atom (carbene, oxygen, fluorine) is transferred *to* or *from* a noncoordinated molecule. We are studying ruthenium complexes with chiral tetradentate PNNP ligands that catalyze such reactions, *e. g.*, the asymmetric cyclopropanation and epoxidation of olefins and the electrophilic hydroxylation and fluorination of 1,3-dicarbonyl compounds [1], [2]:



The structural properties of the intermediates (either carbene or enolato complexes) of the catalytic cycle help explain the observed diastereo- and enantioselectivity. As such intermediates are very reactive, most structural information derives from molecular modeling calculations rather than from crystallographic studies. Nonetheless, crystallography is indispensable as a starting point and to validate the MM methods used.

Carbene transfer from $[RuCl(CHCO_2R)(PNNP)]^+$ to uncoordinated styrene and the attack of electrophilic F- and O-donors onto the enolato complexes $[Ru(O-O)(PNNP)]^{2+}$ ($n = 1$ or 2) will be discussed.

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Keywords: asymmetric catalysis, ruthenium, molecular modeling