

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

#### MS79.29.5

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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

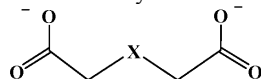
#### MS80.29.1

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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.

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**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

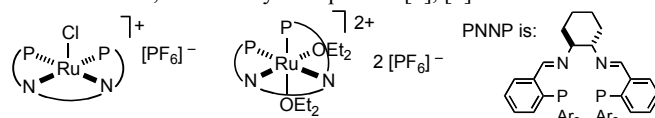
#### MS80.29.3

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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