

## Magnetism of central and host-shell ions in polyoxopalladates

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Polyoxopalladates (POPds) are a new class of nanoscale materials with well-defined structures and are very attractive either for fundamental research or *e.g.* catalysis applications. A cuboid-shaped palladium-oxo shell can adopt a variety of d-ions or lanthanides in its centre while the whole nanocluster can be stabilized by different heterogroups like {PO<sub>4</sub>}, {AsO<sub>4</sub>}, {PhAsO<sub>3</sub>}, *etc* [1, 2]. Electronic and magnetic properties of central metal ions and Pd<sup>2+</sup> ions in the shell are very sensitive to their coordination, local distortions and external influences [3]. In this work we confirmed that individual properties of particular ions in POPds can be tailored, and can be further adapted for the needs of modern technology.

X-ray absorption near edge structure (XANES) and its associated X-ray magnetic circular and linear dichroisms (XMCD and XMLD) can provide information about the valence state, magnetic moments and local symmetry of probed ions in an element-specific way, and in some cases can be even site-specific. The shape of XANES spectra reflects the splitting of the energy levels as determined by the crystal field; by a sum-rule based analysis of the XMCD signal the spin and orbital magnetic moments can be assessed; the XMLD signal relates to the magnetic field induced charge asymmetry and can be used for refinement of the crystal field identified by XANES and XMCD.

XANES, XMCD and XMLD spectra for POPds with central Fe or Pd ions were recorded at the Fe L<sub>2,3</sub> and the Pd M<sub>2,3</sub> absorption edges at 4.5K in external magnetic fields up to 6T. The crystal field parameters, valence states and magnetic moments of probed ions were quantified. Particular features of spectra from 3d central ions and palladium ions in different local environments were described through comparison with results of multiplet calculations performed using the CTM4XAS program [4]. In addition, an influence of a soft hydrogen plasma treatment and re-oxidation process on electronic and magnetic properties of Fe and Pd ions was studied.

It was found that POPds with Fe<sup>3+</sup> central ions in the as-prepared states show different XMCD and XMLD signals depending on the type of their capping groups ({PO<sub>4</sub>} or {PhAsO<sub>3</sub>}) and exhibit distinct reduction behaviour under the hydrogen treatment with visible decrease of magnetic moments; the partial re-oxidation with oxygen gas was going easier for POPds stabilized with {PhAsO<sub>3</sub>} heterogroups. The Pd<sup>2+</sup> ions in the central and shell positions bear different magnetic moments due to the different local coordinations; a possible influence of heterogroups on Pd<sup>2+</sup> magnetism and magnetic polarisation associated with hybridized oxygen states is discussed.

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