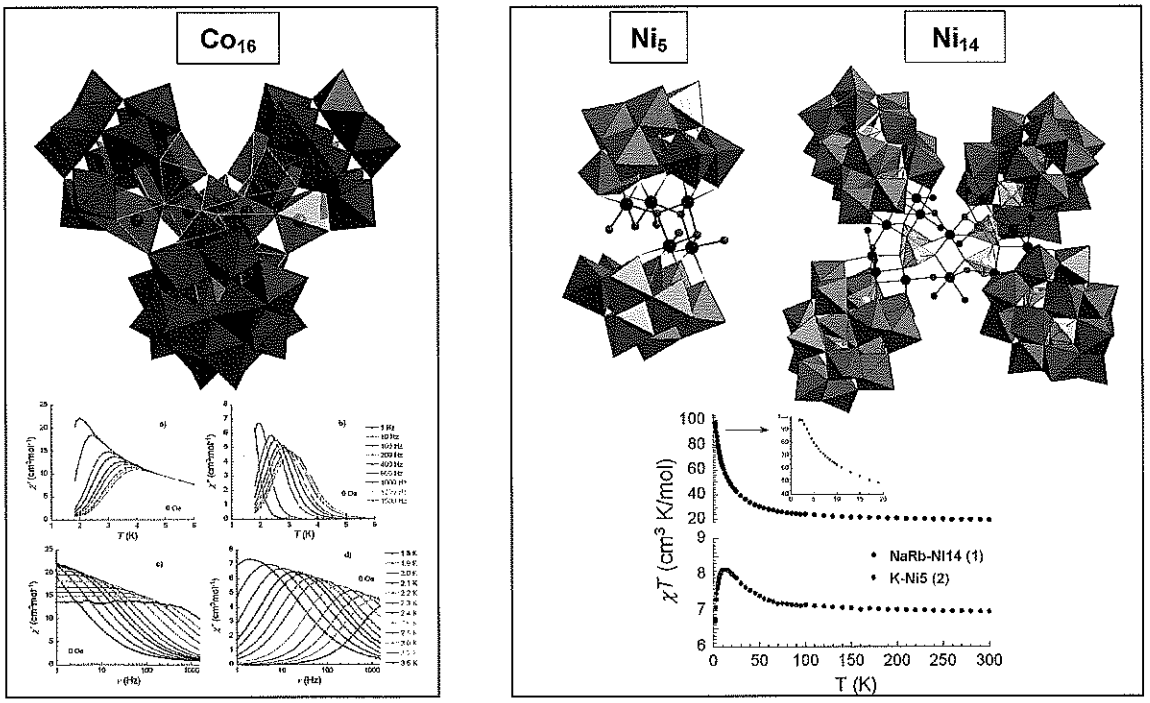
Polynuclear Transition Metal Magnets Based on Polyoxometalates

M. Ibrahim,[a,c] B. S. Bassil,[b] Y. Xiang,[b] Y. Lan,[c] B. Keita,[d] Ulrich Kortz [b]* and Annie K. Powell,[a,c]*

[a] Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany; [b] Jacobs University, School of Engineering and Science, P.O. Box 750 561, 28725 Bremen, Germany; [c] Institute of Inorganic Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstr. 15, D-76131, Karlsruhe, Germany; [d] Laboratoire de Chimie Physique, UMR 8000, CNRS, Equipe d'Electrochimie et de Photoélectrochimie, Université Paris-Sud, Bâtiment 350, 91405 Orsay Cedex, France.

Polyoxometalates (POMs) have been found to be notably versatile inorganic compounds that are being practiced in many fields, e.g., analytical chemistry, molecular magnetism, nanotechnology, medicine, electrochemistry, photochemistry, and catalysis.[1]

It has been a matter of great challenge to encapsulate high nuclearity magnetic core in diamagnetic polyoxometalate shell. As part of our continuous effort to increase number of encapsulated transition metal centres in POMs, that may have interesting magnetic properties and potential applications in catalysis,[2] we have prepared three polyanions, $[\{Co_4(OH)_3PO_4\}_4(A\text{-}\alpha\text{-}PW_9O_{34})_4]^{28-}$ (**Co_{16}**),[3] $[Ni_{14}(OH)_6(H_2O)_{10}(HPO_4)_4(P_2W_{15}O_{56})_4]^{34-}$ (**Ni_{14}**) and $[Ni_5(OH)_4(H_2O)_4(\beta\text{-}GeW_9O_{34})\{\beta\text{-}GeW_8O_{30}(OH)\}]^{13-}$ (**Ni_5**) that encapsulate 16 Co^{II}, 14 Ni^{II} and 5 Ni^{II} centres respectively. These polyanions were synthesized in a simple one-pot reaction in aqueous basic media and were characterized by single-crystal X-ray diffraction, IR spectroscopy, thermogravimetric analysis, elemental analysis, electrochemistry, and magnetic measurements. **Co_{16}** represents the largest cobalt aggregate in polyoxotungstate chemistry, and the first example of a POM based cobalt-core possessing single-molecule magnet behavior. While in case of **Ni_{14}** and **Ni_5** magnetic studies revealed dominant ferromagnetic interactions amongst the nickel(II) ions in both polyanions.



Literature: [1]. M. T. Pope, *Heteropoly and Isopoly Oxometalates* (Springer, Berlin, 1983).[2] U. Kortz, A. Müller, J. Van Slageren, J. Schnack, N. S. Dalal, M. Dressel, *Coord. Chem. Rev.* 2009, **253**, 2315.[3] M. Ibrahim, B. S. Bassil, Y. Xiang, Y. Lan, A. K. Powell, U. Kortz, *Angew. Chem., Int. Ed.* 2011, **50**, 4708.