Crystal Chemistry and Exotic Properties in some Low-D 6th block Transition Metal Phosphates (Cr, Mo, W).

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This presentation focuses on 6th group transition metal phosphates (W, Mo, Cr), characterized by a range of oxidation states from +II to +VI. We will explore the new series of layered monophosphate tungsten bronzes (L-MPTB) $[Ba(PO_4)_2]W_mO_{3m-3}$ ($2 \leq m \leq 5$), consisting of m-layer-thick slabs of WO_6 separated by large spacers. They all show metallic behaviour down to 1.8 K without clear evidence of instability, despite the vicinity of 1D nested topology [1]. Their genuine 2D-character is even more reinforced by the participation of mainly a central W-layers , assigned to anti-polar displacements [2]. Their oxidation under air lead to a series of W and Mo polymorphs that we have using evolutionary crystallographic algorithms (USPEX) and ab-initio DFT calculations. A special attention will be also given to chromium(II) compounds, where the rare Cr^{2+} oxidation state is stabilized by the inductive effect of phosphate groups. This, coupled with the Jahn-Teller effect, gives rise to a variety of frustrated crystal structures and spin-lattice interactions. Besides the non-collinear magnetic structures of α- and β-$Cr_3(PO_4)_2$ the incorporation of large cations (e.g. Ba^{2+}) induces several low-dimensional structures with various exotic features. For instance, the 2D -$Sr_2Cr(PO_4)_2$ compounds exhibits a two-step layer-by-layer magnetic ordering with significant spin-lattice couplings, finally breaking the structural time-reversal symmetry of the room-temperature crystal structure [3].

Reference to a journal publication:

[1] H. Nimoh *et al*., Angew. Chemie Int. Ed. 2023, 62, e202302049.
[2] H. Nimoh *et al.*, JACS 2024, 146, 23955.
[3] H. Nimoh et al., Inorg. Chem. 2024, *63, 21000*