

NOVEL ISOSTRUCTURAL HETEROPOLY SALTS WITH PEACOCK-WEAKLEY TYPE ANION $\text{Na}_9[\text{Ln}(\text{W}_5\text{O}_{18})_2] \cdot 35\text{H}_2\text{O}$ AND THULIUM OR YTTERBIUM HETEROATOMS

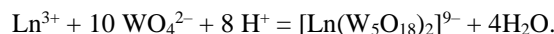
Mariichak Oleksandra Yu.¹, Kaabel Sandra², Karpichev Yevgen A.^{2,3}, Kapitanov Illia V.^{2,3}, Rozantsev Georgiy M.¹, Radio Serhii V.¹

¹Vasyl' Stus Donetsk National University, Ukraine

²Tallinn University of Technology, Estonia

³L.M. Litvinenko Institute of Physical Organic Chemistry & Coal Chemistry NAS of Ukraine
o.mariichak@donnu.edu.ua

Isostructural neutral sodium heteropoly decatungstolanthanidates(III) $\text{Na}_9[\text{Ln}(\text{W}_5\text{O}_{18})_2] \cdot 35\text{H}_2\text{O}$ (Ln = Tm (**SI**), Yb (**SII**)) with Peacock-Weakley type anion and Tm, and Yb as heteroatoms were synthesized using procedure, described in [1]. The compounds were obtained as colorless crystals from the aqueous solutions acidified up to $Z=0.8$ ($Z=v(\text{H}^+)/v(\text{WO}_4^{2-})$) from $\text{Ln}(\text{NO}_3)_3 - \text{Na}_2\text{WO}_4 - \text{HNO}_3 - \text{H}_2\text{O}$ systems. The formation of the salts is going according to the reaction:



The salts were characterized by elemental analysis, FT-IR spectroscopy, and single crystal X-ray diffraction analysis. The latter confirmed that the compounds have Peacock-Weakley type anion, and they are isostructural. There is one case of isostructurality of acidic double salts $\text{K}_3\text{Na}_4\text{H}_2[\text{Ln}(\text{W}_5\text{O}_{18})_2] \cdot (21-22)\text{H}_2\text{O}$ (Ln = Pr, Nd, Sm, Gd, Tb, Dy), which crystallize in a monoclinic crystal system, in space group $P2_1/n$ [2]. Isolated salts with Tm and Yb heteroatoms belong to the second group represented by neutral salts $\text{Na}_9[\text{Ln}(\text{W}_5\text{O}_{18})_2] \cdot 35\text{H}_2\text{O}$ (Ln = Y, Nd, Eu [3], Tb, Dy, Ho, Er [4]), which crystallize in a triclinic space group $P-1$.

$\text{Na}_9[\text{Ln}(\text{W}_5\text{O}_{18})_2] \cdot 35\text{H}_2\text{O}$ (Ln = Tm, Yb) consists of decatungstolanthanidate(III) anion, eight octahedrally coordinated Na^+ cations, one tetragonal-pyramidal Na^+ cation, and 35 H_2O molecules. The decatungstolanthanidate(III) anion is comprised of two $[\text{W}_5\text{O}_{18}]^{6-}$ lacunary units, which coordinate to a central Tm^{3+} or Yb^{3+} cation in the form of square antiprism.

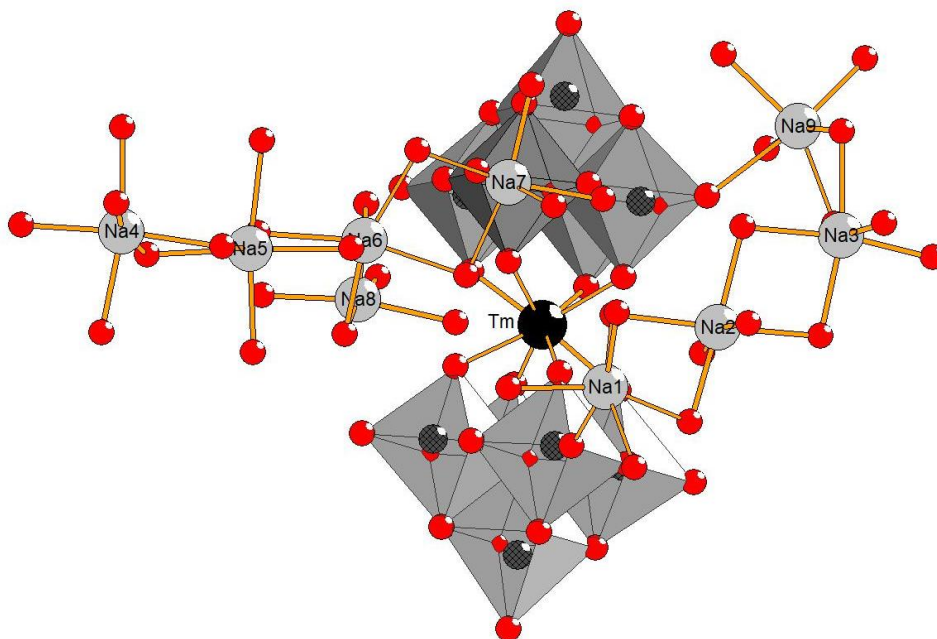


Fig. 1. Crystal structure of $\text{Na}_9[\text{Tm}(\text{W}_5\text{O}_{18})_2] \cdot 35\text{H}_2\text{O}$ (**SI**) (in (**SII**) position of Tm is occupied by an Yb atom)

Acknowledgements. The study was carried out within the Fundamental Research Programme funded by the Ministry of Education and Science of Ukraine (Project No. 0119U100025).

- [1] O.Yu. Mariichak, E.S. Ivantsova, G.M. Rozantsev et al., Thulium-containing heteropoly tungstate with Peacock-Weakley anion: synthesis, properties, and surface micromorphology, *Voprosy Khimii i Khimicheskoi Technologii*, **3**, 38 (2015).
[2] T. Ozeki, T. Yamase, Effect of Lanthanide Contraction on the Structures of the Decatungstolanthanoate Anions in $\text{K}_3\text{Na}_4\text{H}_2[\text{LnW}_{10}\text{O}_{36}] \cdot n\text{H}_2\text{O}$ (Ln= Pr, Nd, Sm, Gd, Tb, Dy), *Crystals Acta Cryst.*, **B50**, 128 (1994).
[3] Y. Yan, B. Li, W. Li et al., Controllable vesicular structure and reversal of a surfactant-encapsulated polyoxometalate complex, *Soft Matter* **5**(20): 4047 (2009).
[4] M. Vonci, M.J. Giansiracusa, W. Van den Heuvel et al., Magnetic excitations in polyoxotungstate-supported lanthanoid single-molecule magnets: An inelastic neutron scattering and ab initio study, *Inorg. Chem.*, **56**, 378 (2017).