

Pr-, Nd-, and Eu-Containing Heteropoly Tungstates With Peacock–Weakley Anion: Synthesis From Aqueous-Acetone Media, FT-IR Spectroscopy, and Surface Micromorphology

Oleksandra Mariichak^{1,2}, Mariia Shevchenko², Georgiy Rozantsev^{1,2}, Serhii Radio^{1,2}

1. Unit for Research, Research Group in Inorganic Chemistry, Vasyl' Stus Donetsk National University, UKRAINE, Vinnytsia, vul. 600-richchia 21, E-mail: o.mariichak@donnu.edu.ua

2. Faculty of Chemistry, Department of Inorganic and Analytical Chemistry, Vasyl' Stus Donetsk National University, UKRAINE, Vinnytsia, vul. 600-richchia 21-215, E-mail: radio@donnu.edu.ua

Abstract – The conditions for the synthesis of pure inorganic sodium heteropoly decatungstometalates (III) – $\text{Na}_9[\text{Pr}(\text{W}_5\text{O}_{18})_2]\cdot 34.25\text{H}_2\text{O}$, $\text{Na}_9[\text{Nd}(\text{W}_5\text{O}_{18})_2]\cdot 34\text{H}_2\text{O}$, and $\text{Na}_9[\text{Eu}(\text{W}_5\text{O}_{18})_2]\cdot 34\text{H}_2\text{O}$, from the aqueous solution of sodium tungstate acidified to $Z=0.80$ with a ratio $\nu(\text{Ln}):\nu(\text{W})=1:10$ and with acetone admixture were established. Isolated salts were analyzed using Elemental Analysis, FT-IR spectroscopy, and Scanning Electron Microscopy

Keywords – Praseodymium, Neodymium, Europium, polyoxotungstate, heteropoly anion, Peacock-Weakley structure.

I. Introduction

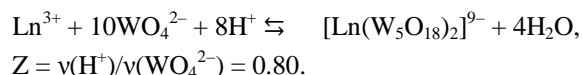
The present work presents the results of synthesis of heteropoly compound with Peacock-Weakley [1] type anion $\text{Na}_9[\text{Ln}(\text{W}_5\text{O}_{18})_2]\cdot n\text{H}_2\text{O}$, which was carried out by the self-assembly from WO_4^{2-} and Ln^{3+} ($\text{Ln}=\text{Pr}, \text{Nd}, \text{Eu}$) in an acidified aqueous solutions; it also studies its structures by FT-IR spectroscopy, and surface micromorphologies by Scanning Electron Microscopy.

II. Experimental Part

In the study, $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$, HNO_3 , $\text{Pr}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, Eu_2O_3 (all are ACS reagent grade) aqueous solutions were used. The $\text{Eu}(\text{NO}_3)_3$ solution was prepared by dissolving Eu_2O_3 in HNO_3 . Excess amount of HNO_3 was removed by two-fold evaporation until wet residue was formed, which then was dissolved in distilled water.

The synthesis of $\text{Na}_9[\text{Ln}(\text{W}_5\text{O}_{18})_2]\cdot n\text{H}_2\text{O}$ was carried out as following. Sodium tungstate solution was added to distilled water, and then HNO_3 solution was added dropwise with vigorous stirring. After that $\text{Ln}(\text{NO}_3)_3$ solution was added dropwise very slowly with vigorous stirring. It bears mentioning that each next drop of $\text{Ln}(\text{NO}_3)_3$ was added only after the disappearance of opalescence from the previous drop. The volume of the final aqueous solution amounted to 100 mL. Adding of reactants corresponds to the stoichiometry of the reaction,

during which heteropoly decatungstolanthanide(III) anions are formed [2]:



In order to isolate salt with the resulting anion as a crystalline precipitate, 100 mL of acetone was added to the solution. Then, the resulting product was sealed and stored for 3 days at 6 °C that led to the formation of needle-like (or plate in case of a salt with Europium) crystalline precipitate.

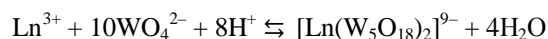
Instrumental methods of analysis.

FT-IR spectroscopy. FT-IR spectroscopy was used to identify anion in the synthesized salt. FT-IR spectra of the air-dry samples of salts were recorded on FTIR Spectrum BXII (Perkin-Elmer), within the wavenumber range of 400–4000 cm^{-1} . For this, a weighed amount of salts (0.0030 g) were triturated with crystalline KBr (0.6000 g) and compressed into a thin disk.

Microscopic analysis. Microscopic study was conducted by scanning electron microscopy (SEM) with microscope JSM-6490LV (JEOL). Air-dry samples deposited on a conductive graphite scotch tape were studied in backscattered electron (BEC) mode used for the elemental analysis of phases being the parts of the sample, and in secondary electron (SEI) mode used to study the surface of the resulting salts. Elemental analysis during the microscopic studies were performed with energy-dispersive X-ray spectrometer INCA PentaFETx3 (OXFORD Instruments).

III. Results and their Discussion

Acidity $Z = 0.80$ in the presence of stoichiometric amounts of reactive ions corresponds to the formation of heteropoly decatungstometalate(III) anions:



(Ln – Yttrium or lanthanides).

To isolate such particles with Pr(III), Nd(III), and Eu(III) ions-heteroatoms, sodium tungstate solutions ($C_w=0.1$ mol/L) acidified to $Z = 0.80$ were used, to which $\text{Ln}(\text{NO}_3)_3$ solutions were added with vigorous stirring. After mixing of the components in a stoichiometric ratio of $X:W=1:10$, acetone were added to the systems (up to 50 vol. %) and formation of needle-like (or plate in case of a salt with Europium) crystalline precipitates were observed. Products yield were ~90%; loss amounting to ~10% were lost likely caused by the solubility of salt when washing the precipitate with water-acetone mixture (1:1) during its separation from the mother liquor. According to the results of the chemical analysis and EDX the isolated precipitates were assigned formulas $\text{Na}_9[\text{Pr}(\text{W}_5\text{O}_{18})_2]\cdot 34.25\text{H}_2\text{O}$, $\text{Na}_9[\text{Nd}(\text{W}_5\text{O}_{18})_2]\cdot 34\text{H}_2\text{O}$, and $\text{Na}_9[\text{Eu}(\text{W}_5\text{O}_{18})_2]\cdot 34\text{H}_2\text{O}$.

Nature of stretch and deformation vibrations in the tungsten-oxygen framework within FTIR spectra of air-dry samples of salts (Fig. 1) also indicates to the presence of Peacock-Weakley heteropoly anion of 10th row in them.

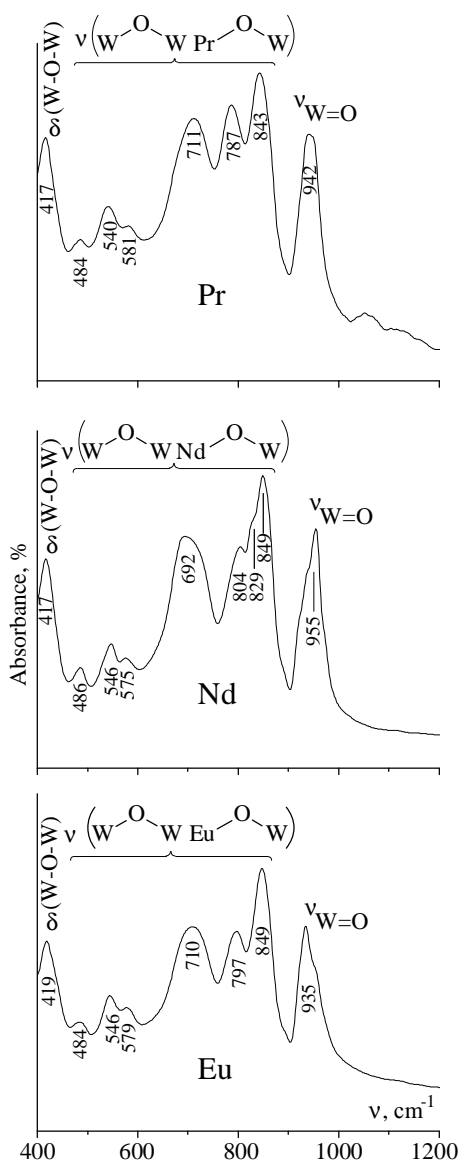


Fig. 1. FT-IR spectra of crystalline salts with $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{9-}$ anion.

In this anion, two lacunar tetradentate pentatungstate-anions $[\text{W}_5\text{O}_{18}]^{6-}$ are coordinated to Ln-heteroatom, thus forming a coordination polyhedron in the shape of a square antiprism.

Microscopic analysis showed that the surface of grains in the isolated salts has fuzzy blurred edges. The size of the grains for the triturated in agate mortar sample of $\text{Na}_9[\text{Ln}(\text{W}_5\text{O}_{18})_2] \cdot 34\text{H}_2\text{O}$ is within the range of 200–400 nm (Fig. 2).

Uniform surface contrast in backscattered electron (BEC) mode points to single-phasesness of the isolated salt (Fig. 3).

On the micrographs of the salt powder in characteristic X-ray emission there are no regions with different surface morphology, and there is an even distribution of Ln (Pr or Nd or Eu), Na, W, O, without segregations and eliquations. These clearly indicate the formation of single-phase samples.

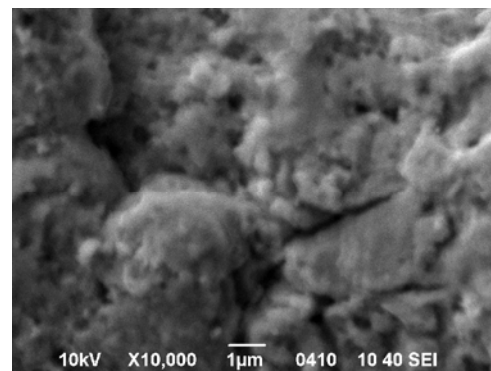


Fig. 2. SEM image of $\text{Na}_9[\text{Eu}(\text{W}_5\text{O}_{18})_2] \cdot 34\text{H}_2\text{O}$ powder surface.

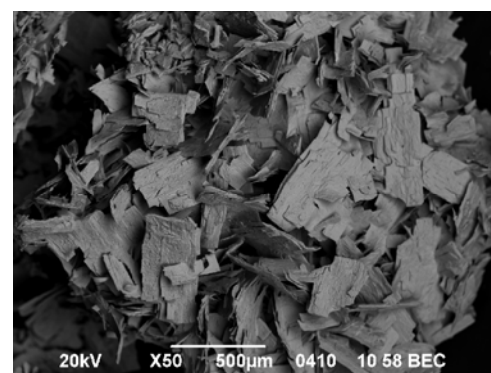


Fig. 3. SEM-image of $\text{Na}_9[\text{Eu}(\text{W}_5\text{O}_{18})_2] \cdot 34\text{H}_2\text{O}$ powder surface in backscattered electron mode ($\times 50$ times)

Conclusion

The conditions for the synthesis of a new pure inorganic heteropoly tungstates $\text{Na}_9[\text{Ln}(\text{W}_5\text{O}_{18})_2] \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Pr}$ ($n=34.25$), Nd ($n=34$), Eu ($n=34$)) from the aqueous solution, acidified to $Z=v(\text{H}^+)/v(\text{WO}_4^{2-})=0.80$ with acetone adding, were determined. FT-IR spectroscopy was used to show that the anion within the synthesized salt has a Peacock-Weakley structure. Scanning electron microscopy confirmed the single-phasesness of the synthesized salts.

Acknowledgements

The study was carried out within the Fundamental Research Programme funded by the MES of Ukraine (Project No. 0116U002521).

References

- [1] R. D. Peacock, T. J. R. Weakley, "Heteropolytungstate Complexes of the Lanthanide Elements. Part I. Preparation and Reactions", *J. Chem. Soc. A.*, pp.1836-1839, 1971.
- [2] O. Yu. Mariichak, E. S. Ivantsova, G. M. Rozantsev, et al. "Thulium-Containing Heteropoly Tungstate With Peacock-Weakley Anion: Synthesis, Properties, And Surface Micromorphology", *Vopr. Khimii Khim. Tekhnologii*, № 3, pp.38-44, 2015.