

STRUCTURE AND PROPERTIES OF TETRAPROPYLAMMONIUM PERTECHNETATE AND PERRHENATE

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TcO₂, Tc₂S₇ or NH₄TcO₄ were first compounds proposed to prepare technetium precipitate before its conversion into metal. In this work we have tested tetrapropylammonium (Pr₄N⁺) salts as providing the waste which could be easily incinerated. Pr₄NTcO₄ was firstly prepared by Roberts [1], who reported its solubility in water as 7.8·10⁻³ M. These measurements were extended for acidic and alkaline media in [2], together with some preliminary studies of thermal properties of (C_nH_{2n+1})₄NXO₄ (X = Tc, Re) and methods of their conversion into metals. Here we present solubility, structural and thermal behaviour data for Pr₄NXO₄ (X = Tc, Re). Starting NH₄⁹⁹TcO₄ was supplied by VO “ISOTOPE”, Russia. Derivatograph Q1500 (Hungary) and an original thermo-balance were used for the TGA and DTA. For solubility measurements we used β-scintillation relative counting of ⁹⁹Tc at Beckman-5000 in K-free vials and GL scintillation cocktail for Tc and ICP/AES measurements at “Plasma 400” Perkin Elmer spectrometer for Re.

For all of the (C_nH_{2n+1})₄NXO₄ where n = 1, 2, 4 Tc and Re salts were isostructural [3]. Therefore, in “cold tests”, Pr₄NReO₄ was synthesized and characterized by X-ray diffraction. The X-ray single crystal structural investigation of Pr₄NReO₄ was carried out at -120°C (Nonius Kappa CCD diffractometer, λMoKα, graphite monochromator). Crystal data: orthorhombic, space group *Pna*2₁, Z = 4, a = 13.169(2), b = 12.311(2), c = 10.107(1) Å; R(F) = 0.0191, R_w(F²) = 0.0461. The Re-O distances are 1.677(12), 1.704(5), 1.719(4) and 1.739(11) Å. Every anion in this structure has four cation neighbours with Re...N distances from 5.06 to 5.34 Å (Fig. 1). Thermal expansion of Pr₄NReO₄ in the range -120°C – 0°C is monotonic, showing no phase transitions (Fig. 2). The linear expansion coefficients are 7.37(18)·10⁻⁵, 1.040(8)·10⁻⁴ and 3.02(11)·10⁻⁵ °C⁻¹ for a, b and c directions, respectively. Anisotropic character of thermal expansion can be explained by the packing of the ions in the crystal structure: it is seen in Fig. 1, that two of the four short contacts between anions and cations are in c direction, that with the lowest thermal expansion coefficient.

The temperatures of phase transitions in Pr₄NReO₄ (Fig. 3) are listed below. Similar phases were identified for Pr₄NTcO₄ by DTA measurements 25 - 179°C (α), 180 - 195°C (β),

195 - 234°C (γ), 234 - 280°C (liquid), indicating that Pr_4NTcO_4 and Pr_4NReO_4 are isostructural. Powder diffraction patterns of Pr_4NReO_4 at 175°C (intermediate β -phase) and 200°C (high temperature γ -phase) have been indexed using CRYSFIRE indexing suite [4]. The intermediate phase can be indexed as tetragonal with $a = 12.271(13)$, $c = 10.823(7)$ Å (possible space group $P4_2/n$). The high temperature phase is hexagonal with $a = 9.749(3)$, $c = 11.654(2)$ Å (possible space group $P6_3/mmc$).

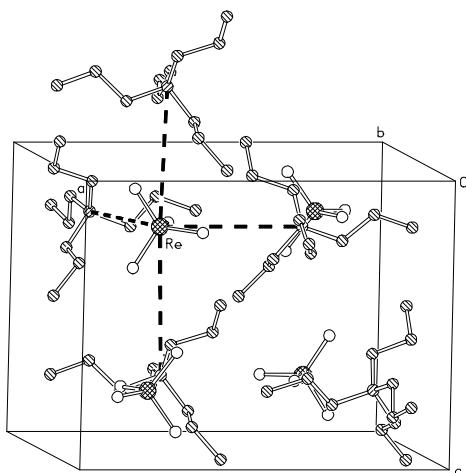


Fig. 1. Unit cell of Pr_4NReO_4 structure. Heavy dashed lines show short $\text{Re}\dots\text{N}$ distances.

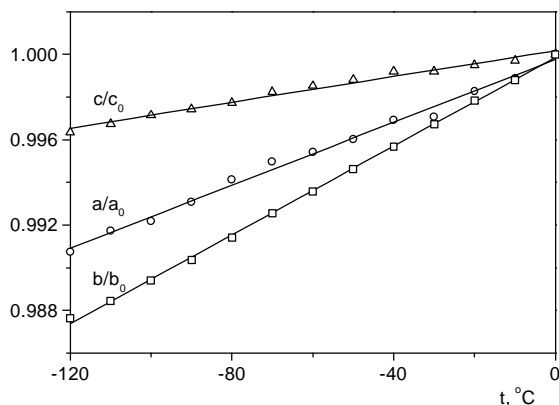


Fig. 2. Temperature dependence of unit cell constants for Pr_4NReO_4 .

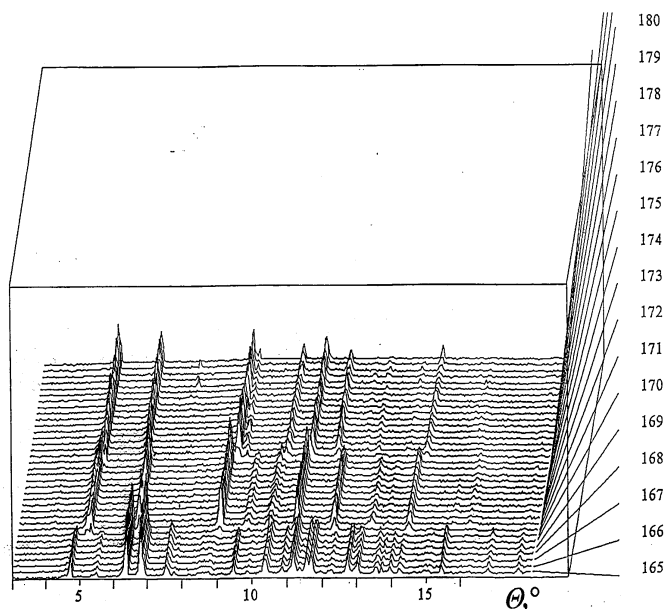


Fig. 3. Thermal phase transitions in Pr_4NReO_4 . Stability intervals as determined by X-ray/DTA, °C:
 α [-120 – 171/186],
 β [171 – 185/199],
 γ [185 – 426],
 liquid [246 – 296].

For solubility measurements the suspensions of each salt in the corresponding electrolyte solution were equilibrated till no changes in radioactivity of solution could be detected. The influence of $[\text{HNO}_3]$, as well as of $[\text{Pr}_4\text{NOH}]$ on the solubility was determined (Fig. 4). Solubility of Pr_4NTcO_4 is approximated as: $[\text{Pr}_4\text{NTcO}_4]_{\text{aq}} = 0.063/[\text{Pr}_4\text{N}^+] + 0.8628$ ($R^2 = 0.98$). Solubility product $\text{SP}(\text{Pr}_4\text{NTcO}_4) = 0.000193 \text{ M}^2/\text{L}^2$. Association constant K_1 of

(Pr₄N⁺)...(TcO₄⁻) in water and Pr₄NOH solutions is $K_1 = 2.6 \pm 0.4$ L/M. The solubility of Pr₄NTcO₄ practically does not depend on the ionic strength of the solution but increases with the acidity of the solution in the same manner as it was shown earlier for Bu₄TcO₄ [5].

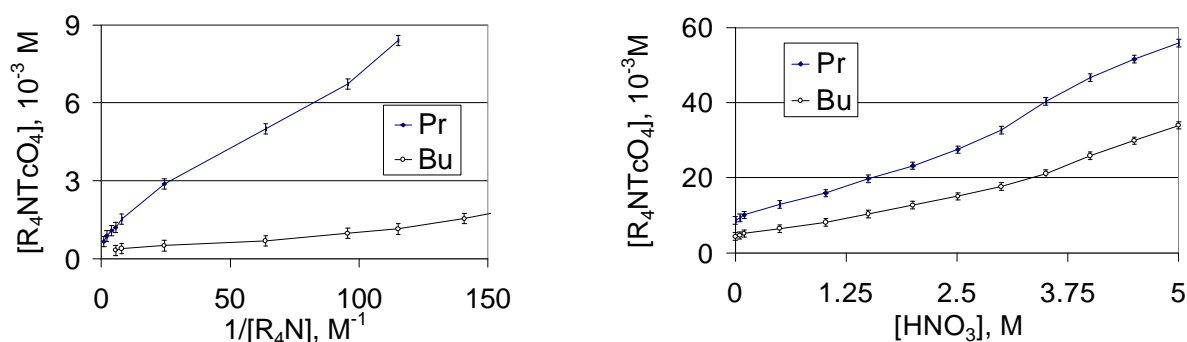


Fig. 4. Solubility of Pr₄NTcO₄ and Bu₄TcO₄ in R₄NOH (left) and HNO₃ (right).

Simulated RW solutions for precipitation studies contained $(2.0 - 7.5) \cdot 10^{-2}$ M/L Tc in $(3 - 4)$ M/L HNO₃, $(2.0 - 7.5) \cdot 10^{-8}$ M/L ²³⁹PuO₂(NO₃)₂ and $5.7 \mu\text{Ci/L}$ ¹⁰⁶Ru(NO)(NO₃)₃. These solutions were denitrificated to $(1-1.2)$ M HNO₃ with HCOOH. In some runs control treatment with 0.2 M H₂O₂ at 60°C gave no change in [Tc] indicating that Tc(VII) is present constantly. Tc was precipitated in form of Pr₄NTcO₄ by titration with 0.98 M Pr₄NOH. Decontamination factors from ²³⁹Pu and ¹⁰⁶Ru were $(0.5 - 1.5) \cdot 10^{-2}$ and $(6.0 - 7.5) \cdot 10^{-2}$ correspondingly. Tc yield varied within $70 - 85\%$ which was less than in case of Bu₄NTcO₄ [5]. Additional Tc recovery was possible with Re as carrier similar to [6].

The thermal properties of Pr₄NTcO₄ and Pr₄NReO₄ were tested by DTA/DTG. Both compounds decompose into technetium carbide or metal by thermal decomposition in argon or (argon + 6% hydrogen gas mixture) correspondingly. The gaseous products were eliminated with gas carrier and analyzed by mass spectrometry indicating presence of H₂O, CO₂, Pr₃N and small amounts of other products due to partial oxidative destruction of cation.

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