

NEW MIXED-VALENCE NEPTUNIUM COMPOUNDS

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Two neptunium molybdate compounds with outersphere guanidinium cations ($\text{HGuan}^+ = \text{C}(\text{NH}_2)_3^+$) have been synthesized. The compounds contain simultaneously dioxocations of hexavalent (NpO_2^{2+}) and pentavalent (NpO_2^+) neptunium.

Crystallographic data:

$(\text{HGuan})_3[(\text{Np}^{\text{V}}\text{O}_2)(\text{Np}^{\text{VI}}\text{O}_2)(\text{MoO}_4)_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$: $a = 12.3393(3)$, $b = 12.9270(3)$, $c = 17.3818(3)$ Å, $\beta = 99.249(1)^\circ$, $V = 2736.53(10)$ Å³, sp. gr. $P2_1/n$, $Z = 4$, $R1 = 0.0298$.

$(\text{HGuan})_3[(\text{Np}^{\text{V}}\text{O}_2)(\text{Np}^{\text{VI}}\text{O}_2)(\text{MoO}_4)_3(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$: $a = 11.3515(18)$, $b = 11.7584(18)$, $c = 19.030(3)$ Å, $V = 2540.1(7)$ Å³, sp. gr. $P2_12_12_1$, $Z = 4$, $R1 = 0.0229$.

Both compounds contain anionic layers $[(\text{Np}^{\text{V}}\text{O}_2)(\text{Np}^{\text{VI}}\text{O}_2)(\text{MoO}_4)_3(\text{H}_2\text{O})]_n^{3n-}$, guanidinium cations and crystallization water molecules are placed between the layers. Three crystallographically independent molybdate-ions are tridentate-bridging between three neptunium atoms. The atoms of penta- and hexavalent neptunium occupy separate positions and have the same coordination number 7, but differ significantly by Np-O distances. The Np-O distances in dioxocations of hexavalent neptunium are from 1.755 to 1.770 Å, in dioxocations of pentavalent neptunium - from 1.823 to 1.852 Å. The Np-O distances for O atoms of molybdate-ions in the equatorial plane of dioxocations are from 2.321 to 2.406 Å for hexavalent and from 2.415 to 2.461 Å for pentavalent neptunium. The water molecule in both cases is coordinated to Np(V) atom.

In earlier studied¹ mixed-valence neptunium compound $\text{Na}_6[(\text{Np}^{\text{V}}\text{O}_2)_2(\text{Np}^{\text{VI}}\text{O}_2)(\text{MoO}_4)_3] \cdot 13\text{H}_2\text{O}$ the atoms of penta- and hexavalent neptunium also occupy separate positions, but in chloride compound $\text{Cs}_7[(\text{Np}^{\text{V}}\text{O}_2)(\text{Np}^{\text{VI}}\text{O}_2)2\text{Cl}_{12}]$ – the same position².

References

1. Grigor'ev M.S., Fedoseev A.M., Budantseva N.A. Russ. J. Coord. Chem., 2003, 29, 877.
2. Alcock N.W., Flanders D.J., Brown D. J. Chem. Soc. Dalton Trans., 1986, 1403.

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