Mendeleev Communications

Mendeleev Commun., 2027, **37**, in press

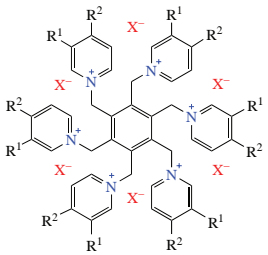
Six-charged pyridinium ligands for TcO_4^- extraction

Zoia A. Sizova, Yuri A. Ustynyuk, Anna Yu. Fominykh, Alexander V. Gopin, Petr I. Matveev, Vladimir G. Petrov and Valentine G. Nenajdenko*

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 932 8846; e-mail: nenajdenko@org.chem.msu.ru

DOI: 10.71267/mencom.8134

Six new water-soluble hexacationic pyridinium receptors for binding pertechnetate anion TcO_4^- were obtained in high yield. Their high susceptibility to the separation of pertechnetate ions in spent nuclear fuel was demonstrated. The extraction feasibility was also mimicked by the use of homologous non-radioactive perrhenate anion ReO_4^-.



Efficient binding of TcO_4^-

Keywords: pyridine, pertechnetate anion, perrhenate anion, extraction, separation, ligand.

Nuclear power's share of the global energy balance is steadily growing year after year. At the same time, the amount of spent nuclear fuel (SNF), whose reprocessing generates highly radioactive waste, is increasing.[1] In accordance with the strategy of closed nuclear fuel cycle in spent nuclear fuel reprocessing,[2] long-lived radionuclides are separated from higly radioactive waste for return to the nuclear fuel cycle, transmutation in fast neutron reactors into short-lived or stable nuclides, or long-term disposal in special matrices. One of the main decay products of ^{235}U in nuclear reactors, the long-lived β-emitter ^{99}Tc ($t_{1/2} = 2.13 \times 105$ years), is stabilized during reprocessing (PUREX) as the pertechnetate anion TcO_4^-. It can be co-extracted with uranium and plutonium during the subsequent reprocessing stages and partially converted into an organic phase.[3,4] In this case, it is present in the entire chain of subsequent technological processes, which essentially complicates the technology and greatly increases its cost.[4–6] Thus, the full extraction of TcO_4^- from nitric acid-containing spent nuclear fuel wastes is a task of primary importance, for which an optimal solution has not yet been found, despite a large amount of research and development in this area.[2,6–14]

Studying the possibility of effective binding of the pertechnetate anion, we have synthesized and investigated a series of water-soluble dicationic receptors of symmetrical structure, in which the pyridinium centers were linked by methylene bridges of varying lengths.[15] It was found that the use of bis-pyridinium salts reduced extraction of pertechnetate into the organic phase by a factor of 3–5. However, those ligands were found to be not efficient enough to completely retain it in the aqueous phase.

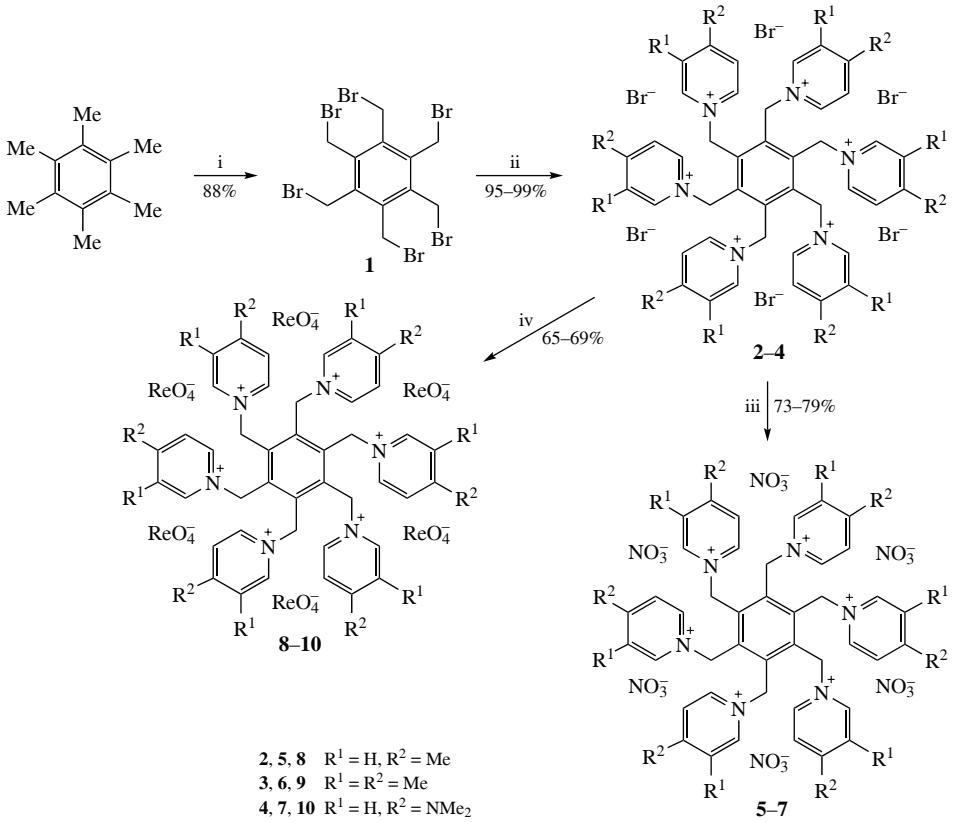
Hoping to improve the pertechnetate extraction suppression coefficient, we decided to examine salts of similar type containing six pyridinium cationic centers attached to the benzene ring *via* methylene groups. Previously, similar receptors containing three, four, and six methylimidazolium fragments[16,17] were found to have a high affinity for TcO_4^-, but due to the insufficient stability of imidazole in a nitric acid medium they were not sufficiently stable for SNF reprocessing. Pyridine derivatives are significantly more stable under these conditions.

Herein, the synthesis of the target compounds was carried out in accordance with Scheme 1. We prepared hexakis(bromomethyl)benzene in 88% yield by bromination of hexamethylbenzene.[18] Next, we found that reactions of **1** with various pyridines occurred under heating in DMF at 80 °C. This allowed us to efficiently obtain pyridinium receptors **2**–**4** in 95–99% yields. High solubility is very important for such receptors. The compounds contained bromide as a counter-anion and were white powders readily soluble in water, methanol, and ethanol, but insoluble in isopropanol, acetonitrile, acetone, ethyl acetate, dichloromethane, chloroform, tetrachloromethane, hexane, benzene, and toluene.

From a technological standpoint, bromides cannot be used in SNF reprocessing since oxidation of the Br^- anion into molecular bromine is possible under such conditions. Therefore, their conversion to nitrates was performed. Ion exchange with silver nitrate leads to complexones **5**–**7** in yields of 73–79%. Their structures were established using ^1H, ^{13}C NMR, and high-resolution mass spectrometry. We also exchanged bromide anions for a non-radioactive analog of pertechnetate, the perrhenate anion ReO_4^-. The interaction of receptors **2**–**4** with sodium perrhenate in water at room temperature (see Scheme 1) produced precipitates of complexones **8**–**10**. Unfortunately, our attempts to obtain crystals suitable for X-ray study were not successful.

The properties of water-soluble ligands **5**–**7** as masking agents were studied in a tributyl phosphate–kerosene system. For all experiments, the concentrations of uranium(VI) and nitric acid in an aqueous phase were 1 and 3 M, respectively. Suppression experiments for pertechnetate anion extraction for ligand **5** were performed at a concentration of 0.4 M, since the complex composition of the solutions within the PUREX process required the most effective suppression of technetium extraction. The extraction suppression coefficient under these conditions was 4.7, and the pertechnetate distribution coefficient was 0.06. These data demonstrated high potential of cationic receptors

© 2027 Mendeleev Communications



Scheme 1 *Reagents and conditions*: i, Br_2, $Br(CH_2)_2Br$; ii, 3-R^1-4-$R^2C_5H_3N$ (6 equiv.), DMF, 80 °C, 27 h; iii, $AgNO_3$ (6 equiv.), H_2O, room temperature; iv, $NaReO_4$ (6 equiv.), H_2O, room temperature.

based on pyridinium fragments for the technology of separating pertechnetate ions in spent nuclear fuel.

The research was supported by The Russian Science Foundation (grant no. 25-23-00050).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.8134.

References

1 *Zelenaya kniga yadernoi energetiki (Green Book of Nuclear Power Engineering)*, ed. E. O. Adamov, JSC NIKIET, Moscow, 2024 (in Russian); https://elib.biblioatom.ru/text/zelenaya-kniga-yadernoy-energetiki_2024.

2 S. V. Gutorova, M. V. Logunov, Yu. A. Voroshilov, V. A. Babain, A. Yu. Shadrin, S. V. Podoynitsyn, O. V. Kharitonov, L. A. Firsova, E. A. Kozlitin, Yu. A. Ustynyuk, P. S. Lemport, V. G. Nenajdenko, A. V. Voronina, V. A. Volkovich, I. B. Polovov, K. N. Dvoeglazov, Yu. S. Mochalov, V. L. Vidanov, V. A. Kascheev, Yu. P. Zaikov, V. A. Kovrov, A. S. Holkina, D. Yu. Suntsov, E. D. Filimonova, O. V. Shmidt, V. I. Volk, A. B. Melentev, K. K. Korchenkin, K. E. German, Yu. A. Pokhitonov, I. G. Tananaev, E. Yu. Pavlyukevich, O. A. Bagautdinova, V. N. Alekseenko, L. N. Podrezova, V. V. Milyutin, N. A. Nekrasova, V. O. Kaptakov, L. I. Tkachenko and S. N. Kalmykov, *Russ. J. Gen. Chem.*, 2024, **94**, S243; https://doi.org/10.1134/S1070363224150015.

3 N. D. Goletskii, B. Y. Zilberman, Y. S. Fedorov, A. S. Kudinov, A. A. Timoshuk, L. V. Sytnik, E. A. Puzikov, S. A. Rodionov, A. P. Krinitsyn, V. I. Ryazantsev and D. V. Ryabkov, *Radiochemistry*, 2014, **56**, 501; https://doi.org/10.1134/S1066362214050099.

4 F. Macasek and J. Kadrabová, *J. Radioanal. Chem.*, 1979, **51**, 97; https://doi.org/10.1007/BF02519927.

5 C. S. Dileep, P. Jagasia, P. S. Dhami, P. V. Achuthan, A. Dakshinamoorthy, B. S. Tomar, S. K. Munshi and P. K. Dey, *Desalination*, 2008, **232**, 157; https://doi.org/10.1016/j.desal.2007.11.053.

6 Y. A. Ustynyuk, N. I. Zhokhova, Z. A. Sizova and V. G. Nenajdenko, *Coord. Chem. Rev.*, 2024, **508**, 215759; https://doi.org/10.1016/j.ccr.2024.215759.

7 K. George, A. J. Masters, F. R. Livens, M. J. Sarsfield, R. J. Taylor and C. A. Sharrad, *Hydrometallurgy*, 2022, **211**, 1052; https://doi.org/10.1016/j.hydromet.2022.105892.

8 C. I. Pearce, R. C. Moore, J. W. Morad, R. M. Asmussen and S. Chatterjee, *Sci. Total Environ.*, 2020, **716**, 132849; https://doi.org/10.1016/j.scitotenv.2019.06.195.

9 E. A. Gendy, D. T. Oyekunle, J. Ali, J. Ifthikar, A. M. M. Ramadan and Z. Chen, *J. Environ. Radioact.*, 2021, **238**–**239**, 106710; https://doi.org/10.1016/j.jenvrad.2021.106710.

10 K. Patra, S. A. Ansari and P. K. Mohapatra, *J. Chromatogr. A*, 2021, **1655**, 462491; https://doi.org/10.1016/j.chroma.2021.462491.

11 C. I. Pearce, E. A. Cordova, W. L. Garcia, S. A. Saslow, K. J. Cantrell, J. W. Morad, O. Qafoku, J. Matyáš, A. E. Plymale, S. Chatterjee, J. Kang, F. C. Colon, T. G. Levitskaia, M. J. Rigali, J. E. Szecsody, S. M. Heald, M. Balasubramanian, S. Wang, D. T. Sun, W. L. Queen, R. Bontchev, R. C. Moore and V. L. Freedman, *Sci. Total Environ.*, 2020, **716**, 136167; https://doi.org/10.1016/j.scitotenv.2019.136167.

12 Y. Xie, L. Yu, L. Chen, C. Chen, L. Wang, F. Liu, Y. Liao, P. Zhang, T. Chen, Y. Yuan, Y. Lu, B. Huang, H. Yang, S. Wang, S. Wang, L. Ma, F. Luo, Y. Liu, B Hu, H. Wang, D. Pan, W. Zhu, N. Wang, Z. Wang, L. Mao, S. Ma and X. Wang, *Sci. China Chem.*, 2024, **67**, 3515; https://doi.org/10.1007/s11426-024-2218-8.

13 Z. Xing, Z. Lai, Q. Sun, C. Xiao, S. Wang, X. Wang, B. Aguila-Ames, P. K. Thallapally, K. Martin and S. Ma, *Chem Bio Eng.*, 2024, **1**, 199; https://doi.org/10.1021/cbe.3c00125.

14 W. Mandal, S. Fajal, A. V. Desai and S. K. Ghosh, *Coord. Chem. Rev.*, 2025, **524**, 216326; https://doi.org/10.1016/j.ccr.2024.216326.

15 Yu. A. Ustynyuk, I. P. Gloriozov, Z. A. Sizova, N. I. Zhokhova, U. M. Leksina, A. Yu. Fominykh, A. V. Gopin, P. I. Matveev, V. G. Petrov, V. A. Tafeenko and V. G. Nenajdenko, *Dalton Trans.*, 2026, **55**, 359; https://doi.org/10.1039/D5DT02176F.

16 P. Ghosh, R. Ghosh and T. K. Ghosh, *Dalton Trans.*, 2020, **49**, 3093; https://doi.org/10.1039/D0DT00365D.

17 R. Ghosh, T. K. Ghosh, S. Pramanik, A. S. M. Islam and P. Ghosh, *ACS Appl. Mater. Interfaces*, 2023, **15**, 25184; https://doi.org/10.1021/acsami.2c19555.

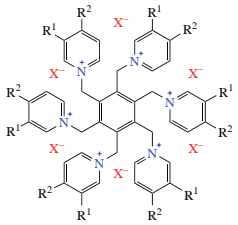
18 Z. Zhang, J.-F. Ma, Y.-Y. Liu, W.-Q. Kan and J. Yang, *CrystEngComm*, 2013, **15**, 2009; https://doi.org/10.1039/C3CE26874H.

Received: 1st July 2026; Com. 26/8134

Contents entry

Six-charged pyridinium ligands for TcO_4^- extraction

Zoia A. Sizova, Yuri A. Ustynyuk,
Anna Yu. Fominykh, Alexander V. Gopin,
Petr I. Matveev, Vladimir G. Petrov,
Valentine G. Nenajdenko



Efficient binding of TcO_4^-