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TITLE OF THE ARTICLE (5-9 words)

Background. ***The research aimed to find a convenient preparative method for the synthesis of tantalum water-soluble complexes from metal oxide, which would not require harsh or hazardous reaction conditions or the use of expensive, less accessible reagents. The application of the triethylamine-hydrogen fluoride complex as an inexpensive and safe surrogate for hydrofluoric acid facilitated the conversion of tantalum oxide into a form suitable for further transformations in aqueous or organic environments under mild conditions and without any restrictions on the use of glassware.***

Methods. ***In this work, a method for dissolution of tantalum pentaoxide, a relatively chemically inert compound, with formation of highly soluble fluoride complex was developed. The variety of techniques were used to identify the complex, such as: IR, UV/Vis and NMR spectroscopy. All materials were of analytical grade and obtained from commercial sources without further purification. The IR spectra of the synthesized compounds were recorded on a Fourier IR spectrometer Perkin-Elmer BX (400-4000 cm^{-1}) in KBr tablets. Electron spectra of diffuse reflection (ESD) of polycrystalline of samples in the UV and visible range were recorded on a Varian spectrometer 5000. The intensity was measured relative to MgO or KBr. The solvents were purified according to the standard procedures. All other starting materials were purchased from commercial sources. ^1H and ^{19}F NMR spectra were recorded on a Varian Gemini 2000 spectrometer.***

Results. ***It was found that old samples of tantalum oxide, inert to most inorganic and organic acids and bases, are easily converted to fluorotantalates by reacting with commercial trimethylamine hydrofluoric acid complex at room temperature within short reaction times. The reaction is easily scaled up to multigram quantities and the product $(NHEt_3)_2[TaF_7]$ is obtained in essentially pure form after operationally simple workup protocol. Bench stable tantalum complex is insensitive to air and moisture.***

Conclusions. ***A developed protocol can serve as a convenient and safe starting point for the preparation diverse coordination and organometallic tantalum compounds both by fluoride ligand substitution and organic cation exchange. Tantalum oxide hydrofluoride-dissolution – precipitation-by-hydrolysis cycle may also be used for crude tantalum sample purification owing to the crystalline nature of the heptafluoride complex and its other physico-chemical properties.***

Keywords***: tantalum, fluorination, complexation, hydrofluoric acid, NMR spectroscopy.***

Background

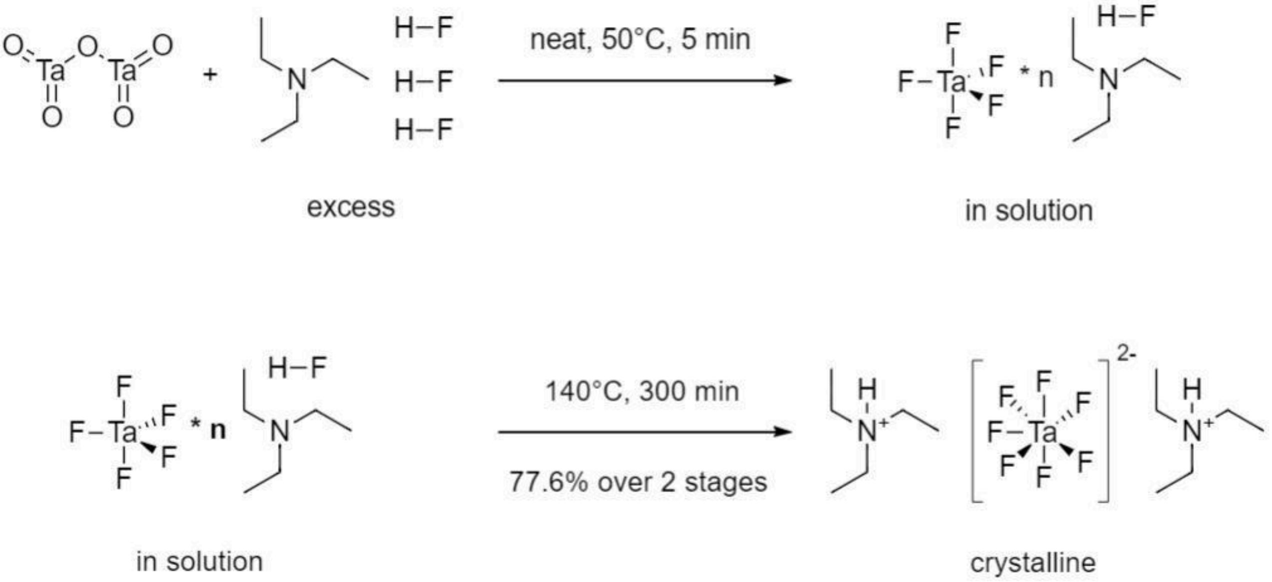
Tantalum, a transition metal, holds significant importance in modern technology and scientific research due to its exceptional properties and versatile applications. This metal finds extensive utilization in various fields, including electronics (McLellan et al., 2023), aerospace engineering (Buckman et al., 2000), and biomedical sciences (Levine et al., 2006). Notably, tantalum capacitors are integral components in electronic devices, while tantalum alloys are favored for their high melting points and corrosion resistance in aircraft and surgical implants. Central to its utility is tantalum's remarkable chemical inertness, both in metallic form and as its oxide. This inertness imparts stability to tantalum components, ensuring prolonged functionality in harsh environments. Tantalum oxide, particularly, possesses exceptional dielectric properties (Hiratani et al., 2002), making it indispensable in microelectronics (Ezhilvalavan et al., 1999) and optoelectronics. However, despite its inert nature, the inherent insolubility of metallic tantalum and its oxide presents challenges in material processing and chemical synthesis. Conventional methods for preparing tantalum complexes often involve harsh conditions or costly reagents, limiting their scalability and practicality. Therefore, the development of novel, simple, and scalable methodologies for the preparation of tantalum complexes is imperative. In this context, the present study introduces a new protocol for the preparation of soluble tantalum fluoride complexes, offering a promising avenue for further exploration and application in diverse research areas.

Methods

All materials were of analytical grade and obtained from commercial sources without further purification. The IR spectra of the synthesized compounds were recorded on a Fourier IR spectrometer Perkin-Elmer BX (400-4000 cm^{-1}) in KBr tablets. The solvents were purified according to the standard procedures (Armarego, 2022). All other starting materials were purchased from commercial sources. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian Gemini 2000 spectrometer.

Results

The synthesis of triethylammonium fluorotantalate $(NHEt_3)_2[TaF_7]$ was carried out according to the following method (Scheme 1). 10.0 grams of tantalum oxide (Ta_2O_5) were placed into a 100 mL round-bottom flask equipped with a magnetic stir bar. To the flask, 50 mL of pure triethylamine trihydrofluoride (ca. 37% HF) was added in one portion. Immediate moderate heating of the mixture ensued. The flask was then immersed in a preheated oil bath maintained at 50°C. The mixture was stirred until a homogeneous, slightly turbid yellowish solution was formed (dissolution took approximately 5 minutes). Afterward, the reaction mixture was transferred into a crystallization dish, which was heated to 140°C for 5 hours until obtaining a gray solid residue. During the evaporation, gaseous HF is generated from triethylamine trihydrofluoride. The crystallization dish was cooled, and 100 mL of dichloromethane was added. The mixture was then filtered to remove insoluble impurities. Dichloromethane was evaporated, and to the residue, 50 mL of diethyl ether was added, followed by vigorous stirring until the formation of fine white crystalline precipitate. The precipitate was filtered, washed on the filter with diethyl ether (3 x 20 mL), pentane (20 mL), and dried under vacuum (1 mbar) to obtain white powder of $(NHEt_3)_2[TaF_7]$ (18.2g, 77.6% yield).



Scheme 1. The synthesis of triethylammonium fluorotantalate $(NHEt_3)_2[TaF_7]$

Powder is indefinitely stable under ambient conditions if stored in closed vessel. The substance exhibits slight hygroscopicity. It readily dissolves in water, methanol, ethanol, dichloromethane, acetone, chloroform, and acetonitrile. It is sparingly soluble in diethyl ether and insoluble in alkanes. It remains stable in aqueous solution at room temperature for at least one day and decomposes upon heating above 200°C. During synthesis, a minor by-product of approximately 15% octafluorotantalate is formed; the formation of TaF_6^- and oxo-complexes was not observed.

Discussion and conclusions

In this work, a method for dissolution of tantalum pentaoxide, a relatively chemically inert compound, with formation of highly soluble fluoride complex was developed. The variety of techniques were used to identify the complex (Fig.1).

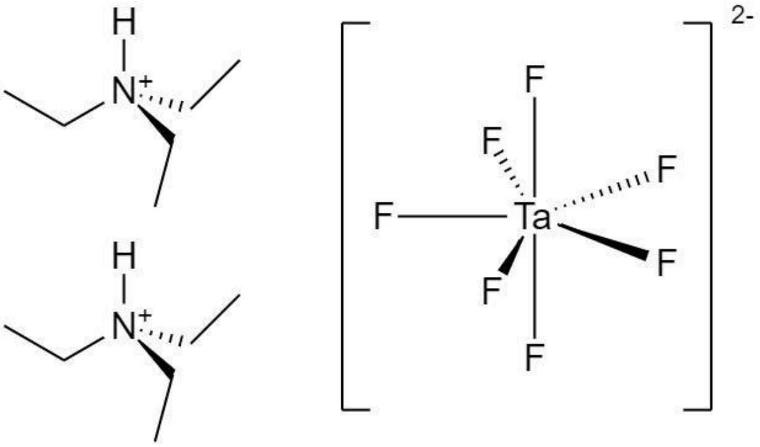


Figure 1: The scheme of triethylammonium fluorotantalate complex $(NHEt_3)_2[TaF_7]$

NMR spectroscopy. ^{1}H NMR (400 MHz, D_2O) δ 1.27 (methyl groups, 18H, t, J = 7.4 Hz), 3.20 (methylene groups, 12H, q, J = 7.4 Hz). ^{13}C NMR (101 MHz, D_2O) δ 46.63, 8.19. ^{19}F NMR (376 MHz, D_2O) δ -130.80 (7F, s). ^{1}H and ^{13}C NMR demonstrate the presence of only triethylammonium. In the crystalline state, $[TaF_7]^{2-}$ polyhedra are single-capped trigonal prisms; in solution, due to the conformational lability of the heptacoordinated complex anion, an equivalence of fluorine atoms on the NMR timescale is expected. A sharp singlet in the ^{19}F NMR spectrum recorded at 25°C (Fig. 2) indicates the presence of the $[TaF_7]^{2-}$ anion as the only fluorine-containing complex. Hydrolisys product's peak (such as Marignac's salt

$K_2[Ta_2O_3F_6]$) is not seen on the spectrum, indicating at least short-term stability of the complex in aqueous solution, potencially owing to the acidic nature of the organic cation.

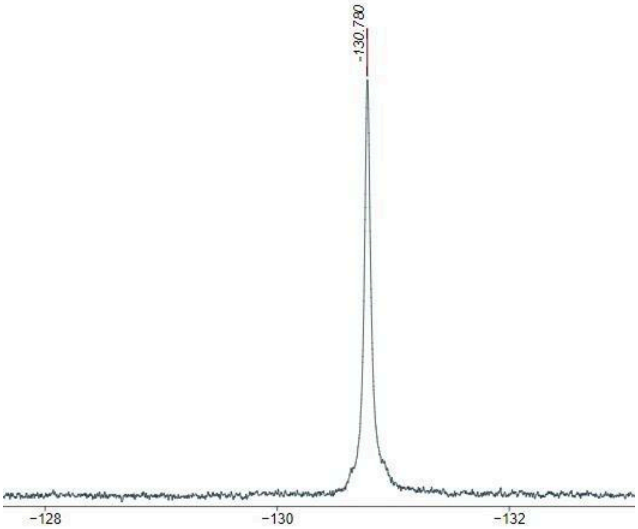


Figure 2: ^{19}F NMR fragment $[TaF_7]^{2-}$ anion of triethylammonium fluorotantalate complex $(NHEt_3)_2[TaF_7]$

IR spectroscopy. Normal vibration analysis of TaF_7^{2-} ion has been performed for the disturbed prism of C_{2V} symmetry and for the pentagonal bi-pyramid having D_{5h} configuration (English et. al.,1983). Infrared (IR) spectrum (Fig. 3, top) displays a strong band at about 530 cm^{-1}: asymmetric valence vibration - (TaF). Ta-F band frequency perfectly matches the literature data concerning alkali metal heptafluorotantalates (for K_2TaF_7 - see (Agulyansky, 2003) – even reported shoulder at 640 cm^{-1} is present (Fig. 3, bottom). In IR spectrum of crude compound before crystallization also TaF_8^{3-} band at about 490 cm^{-1} is present (Fig. 3, bottom). Wide peaks at 3420 cm^{-1} and 1640 cm^{-1}: O-H bond stretching and bending of water; low intensity combination band at 2100 cm^{-1} is also present. NEt_3H^+: 3000 cm^{-1} (s), 2974 cm^{-1} (s), 2938 cm^{-1} (s) – ν(C-H); 2800 cm^{-1} (s), 2738 cm^{-1} (m), 2678 cm^{-1} (s), 2505 cm^{-1} (s) – ν(N-H); 1479 cm^{-1} (m) 1448 cm^{-1} (s), 1394 cm^{-1} (s), 1166 cm^{-1} (s), 1069 cm^{-1} (m), 1031 cm^{-1} (s), 841 cm^{-1} (m), 735 cm^{-1} (w).

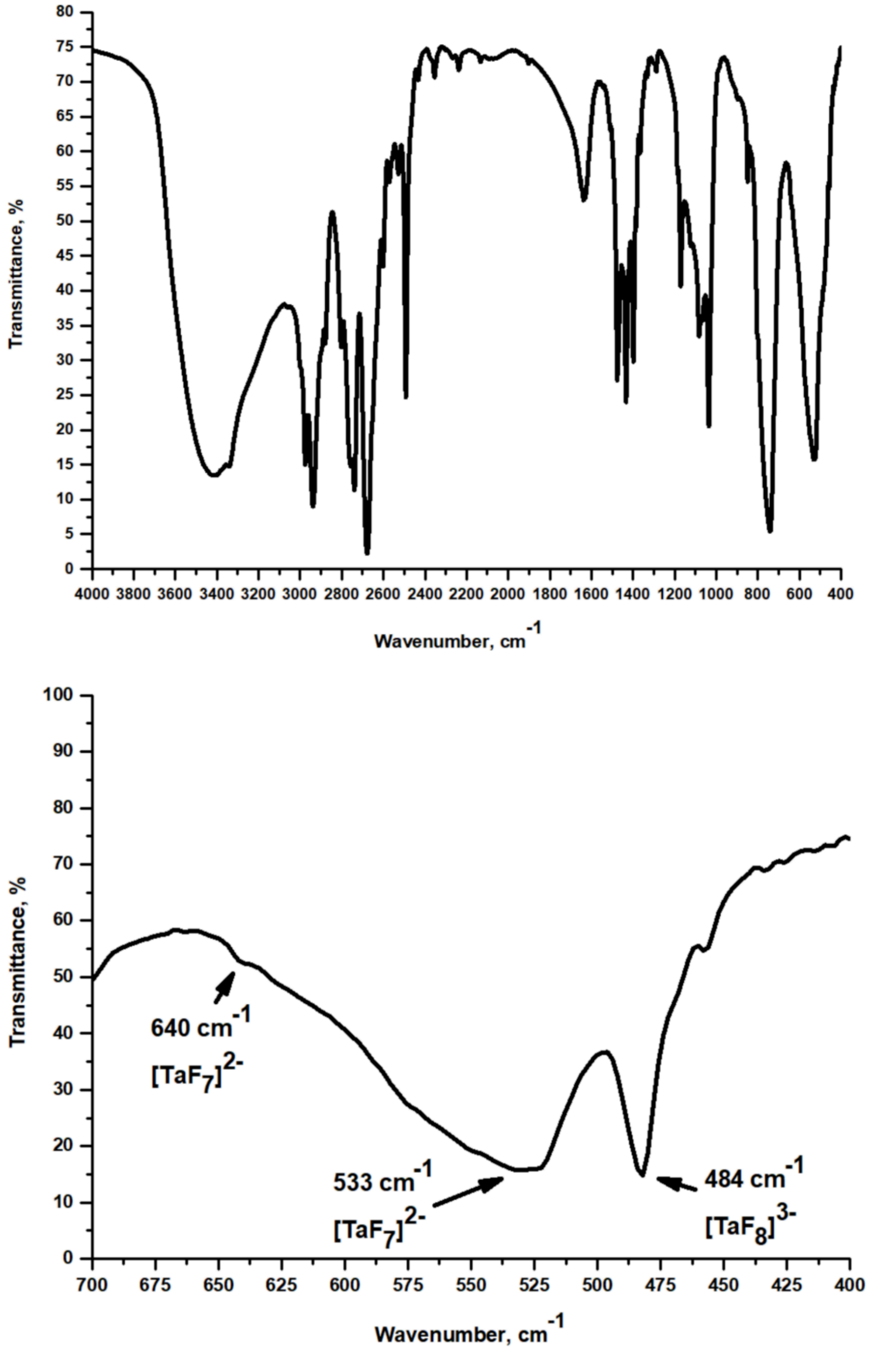


Figure 3. IR spectra of triethylammonium fluorotantalate complex $(NHEt_3)_2[TaF_7]$ and crude mixture

Conventional methods for synthesizing fluorotantalates are based on the use of elemental fluorine, bromine trifluoride (Gutmann et. al., 1950), molten NH_4HF_2 (Kalinnikov et al., 1985), and aqueous solutions of hydrofluoric acid. Each of the previously published methods requires the use of relatively synthetically inconvenient reagents and specialized handling, whereas triethylammonium hydrofluoride is an accessible reagent that is undemanding in terms of storage and application, making it a much more attractive option for use by less experienced specialists or in the absence of specialized equipment and glassware in the laboratory. It is also worth noting that TEA*3HF is a much more familiar reagent to a wide range of inorganic synthetic chemists (eg. (Vergote et al., 2012)) and especially organic chemists (eg. (Gurbanov, 2021; Munoz et al., 2019), which makes the new method for synthesizing fluorotantalates more convenient for them. Fluorotantalates are versative precursors for synthesis of tantalum coordination compounds (Rosenheim et. al., 1932; Dirtu et. al., 2009; Ramos et. al., 2015; Zupanek et. al., 2019), new materials (Boca et. al., 2020) and organotantalum compounds (Kleinhenz et. al., 1998). An operationally simple, scalable protocol for multi-gram scale preparation of soluble form of tantalum, suitable for both aqueous and organic solvents, has been developed. The method does not require the use of expensive reagents, complex equipment, or the use of Teflon vessels. The procedure serves as a convenient alternative to known methodologies involving concentrated hydrofluoric acid or anhydrous hydrogen fluoride. The obtained tantalum complex can be easily purified, remains entirely stable during storage under ambient conditions, and serves as a convenient precursor for the synthesis of new inorganic and organometallic tantalum compounds.

Authors' contribution: Oleksandr Zaporozhets – writing, original draft, conceptualization; Vadim Pavlenko – view and edit, revision.

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НАЗВА СТАТТІ

Вступ. ***Метою дослідження було розробити зручний препаративний метод синтезу водорозчинних комплексів танталу з оксиду металу, який не вимагав би жорстких або небезпечних умов синтезу або використання дорогих, менш доступних реагентів. Застосування комплексу триетиламін-фтористий водень як недорогого та безпечного***

замінника фтористоводневої кислоти сприяло перетворенню оксиду танталу у форму, придатну для подальших перетворень у водному чи органічному середовищах у м'яких умовах і без будь-яких обмежень щодо використання скляного посуду.

Методи. ***У цій роботі розроблено метод розчинення відносно хімічно інертної сполуки пентаоксиду танталу з утворенням добре розчинного фторидного комплексу. Для ідентифікації комплексу було використано різні методи, такі як: інфрачервона, УФ/Вид та ЯМР спектроскопія. Усі матеріали були аналітичного класу та були отримані з комерційних джерел без додаткового очищення. ІЧ-спектри синтезованих сполук записували на ІЧ-фур'є-спектрометрі Perkin-Elmer BX (400-4000 см$^{-1}$) у таблетках KBr. Електронні спектри дифузного відбиття (ESD) полікристалічних зразків в УФ та видимому діапазоні реєстрували на спектрометрі Varian 5000. Інтенсивність вимірювали відносно MgO або KBr. Розчинники очищали за стандартними методиками [13]. Всі інші вихідні матеріали були придбані з комерційних джерел. Спектри ЯМР ^{1}H і ^{19}F записували на спектрометрі Varian Gemini 2000.***

Результати. ***Було виявлено, що старі зразки оксиду танталу, інертні до більшості неорганічних і органічних кислот і основ, легко перетворюються на фтортанталати шляхом реакції з комерційним комплексом триметиламіну плавикової кислоти при кімнатній температурі за короткий час реакції. Реакцію легко масштабувати до мультиграммових кількостей, і продукт $(NHEt_3)_2[TaF_7]$ отримують в основному чистому вигляді після операційно простого протоколу обробки. Стендовий стабільний танталовий комплекс нечутливий до повітря та вологи.***

Висновки. ***Розроблений протокол може служити зручною та безпечною відправною точкою для отримання різноманітних координаційних та металоорганічних сполук танталу як шляхом заміщення фторидного ліганду, так і обміну органічних катіонів. Розчинення гідрофториду оксиду танталу – цикл осадження шляхом гідролізу також може бути використаний для очищення зразків неочищеного танталу завдяки кристалічній природі гептафторидного комплексу та його іншим фізико-хімічним властивостям.***

Ключові слова: ***тантал, фторування, комплексоутворення, фторидна кислота.***