

New Accelerated “Green” Synthesis of a Tungsten–Unithiol Complex

P. D. Kuznetsova^{a,*}, E. A. Mukhanova^a, A. A. Tereshchenko^a,
E. R. Kolomenskaya^a, and A. V. Soldatov^a

^aSouthern Federal University, Rostov-on-Don, Russia

*e-mail: pkuznecova@sfedu.ru

Received December 7, 2023; revised December 25, 2023; accepted December 25, 2023

Abstract—Unithiol, as a biologically active ligand that forms stable complexes with metals, is of significant interest and requires systematic research when designing efficient medicinal agents. The accelerated “green” synthesis of a tungsten complex with unithiol as a ligand is carried out using two methods: ultrasonic and microwave. The precursors to this reaction are an extract of *Picea pungens* Engelm. spruce needles as a natural source of presumably bioactive unithiol and sodium tungstate; the reaction duration is 15 min. X-ray absorption spectra (XANES) near the L_3 edge of tungsten absorption for a tungsten–unithiol complex are obtained and qualitatively analyzed for the first time.

DOI: 10.1134/S2635167623601316

INTRODUCTION

Unithiol is widely used as a detoxicant for heavy metals such as mercury [1], cadmium [2], lead [3], vanadium [4], and even rutherfordium [5], due to its property of binding metal ions into complex compounds. Unithiol complexes are often soluble in water, which makes them convenient for use as a medicinal agent. The extraction of unithiol from natural resources is of particular interest. In the present work, blue spruce is a proven source of unithiol in the synthesis of a unithiol–tungsten complex.

EXPERIMENTAL

Preparation of spruce extract. A 50-g weighing sample of *Picea pungens* Engelm. spruce needles dry-cleaned from external contaminants was wrapped in filter paper and placed in a Soxhlet apparatus. Extraction was carried out with 95% ethyl alcohol for 6 h. The hermetically sealed flask with the extract was stored in a dark place.

Ultrasonic method of synthesis. To obtain a tungsten–unithiol complex, an excess of an ethanolic extract of *Picea pungens* Engelm. spruce needles (40 mL) was added to sodium tungstate dihydrate $\text{Na}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ (0.33 g) in a 100-mL heat-resistant glass. The mixture was stirred for 5 min on a magnetic stirrer at a speed of 400 rpm without heating. At the next stage, the resulting mixture was treated with ultrasound using a VCX-750 homogenizer (Sonics & Materials, the

United States) at the following parameters: time 15 min, frequency 20 kHz, intensity 70 W cm^{-2} , and pulsation with a ratio of the operating time and pausing of 2 : 1. At the end of the reaction, the temperature of the mixture was $\sim 50^\circ\text{C}$. Next, the reaction product was precipitated by centrifugation at 10000 rpm for 10 min, then the sediment was washed with 96% ethyl alcohol and centrifuged at the same parameters, and dried at a temperature of 60°C .

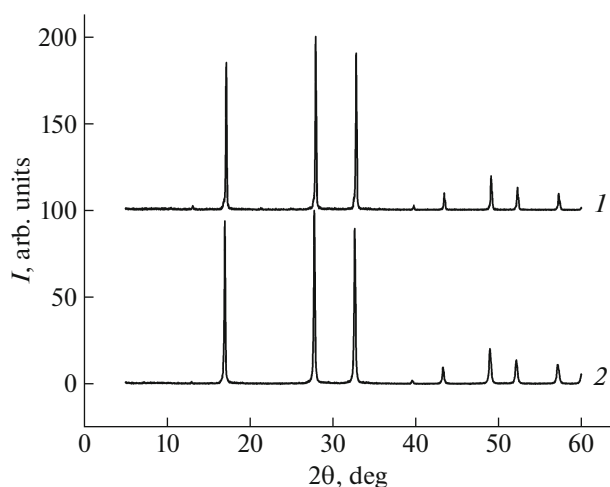


Fig. 1. X-ray powder diffraction profiles of the unithiol–tungsten complexes synthesized by the (1) ultrasonic and (2) microwave methods.

Table 1. Elemental composition of the needles of *Picea pungens* Engelm.

Element	Normalized content, wt %
Ca	36.28
K	32.30
Si	14.64
Al	5.13
S	3.03
Co	2.87
Fe	2.04
P	1.96
Mn	0.95
Ti	0.38
Zn	0.35
Cu	0.07
Σ	100

Microwave method of synthesis. In preparation for the synthesis of a tungsten–unithiol complex, 0.1 g of sodium tungstate dihydrate was weighed in a microwave reactor, and an ethanolic extract of the *Picea pungens* Engelm. spruce needles (10 mL) was added. A 0.15-g weighing sample of PEG-1000 was added to increase the boiling point of the alcohol solution and prevent it from reaching critical pressure due to its boiling. To homogenize the mixture, it was stirred for 5 min on a magnetic stirrer at 400 rpm without heating. At the next stage, the mixture was placed in a quartz cell for microwave synthesis. The reaction time in a CEM Discover SP reactor (CEM Corporation,

the United States) was 15 min at a set temperature of 110°C with constant stirring with a stir bar. After cooling to room temperature, the reaction product was precipitated by centrifugation at 10000 rpm for 10 min, decanted, washed with 96% ethyl alcohol, centrifuged again, and dried at 60°C.

The methods used make it possible to reduce the reaction time from three–four days [6] to 15 min.

RESULTS AND DISCUSSION

X-ray diffraction phase analysis. X-ray diffraction plots were obtained on a Bruker D2 Phaser diffractometer (Bruker Corporation, Germany). According to X-ray phase analysis (Fig. 1), the samples are single phase and the peaks in the X-ray diffraction pattern correspond to the data from PDF-2 under number 00-045-1784, $C_{12}H_{32}Na_4O_{17}S_{12}W_2 \cdot 3H_2O$ [6].

X-ray fluorescence analysis. The element content was studied using a Bruker M4 Tornado instrument (Bruker Corporation, Germany). The elemental composition of blue-spruce needles is presented in Table 1; the content of tungsten, sodium, and sulfur in the synthesized complexes, in Table 2; the information is also presented graphically in Fig. 2.

X-ray absorption spectroscopy. X-ray absorption spectra in the XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) regions were measured beyond the L_3 absorption edge of tungsten at the structural-materials science station of the Kurchatov synchrotron-radiation source [7] and are shown in Fig. 3. Samples were prepared as powders densely applied to Kapton. In order to calibrate the energy scale of the recorded spectra, simultaneously with the absorption spectra of the samples under study, we recorded the absorption spectrum of a pellet of a reference sample, tungsten oxide WO_3 , located between the second and third ionization chambers. The spectra were normalized and the energy calibrated using the Athena program included in the DEMETER software package [8].

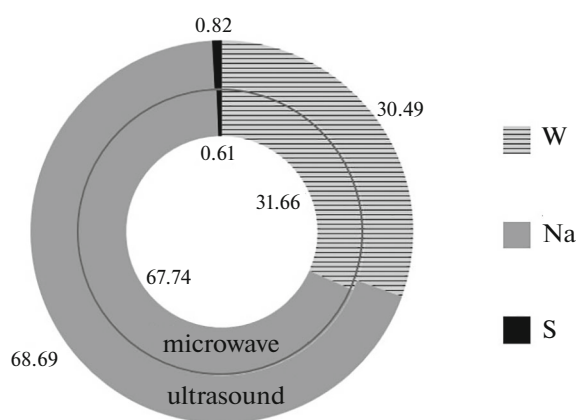


Fig. 2. Pie charts of the sodium, tungsten, and sulfur contents in the unithiol–tungsten complexes obtained by the microwave and ultrasonic methods (based on elemental analysis by X-ray diffraction).

Table 2. Elemental composition of the unithiol–tungsten complexes obtained by the ultrasonic- and microwave-synthesis methods

Element	Atomic number	Content, at %	
		ultrasonic	microwave
W	74	30.49	31.66
Na	11	68.69	67.74
S	16	0.82	0.61

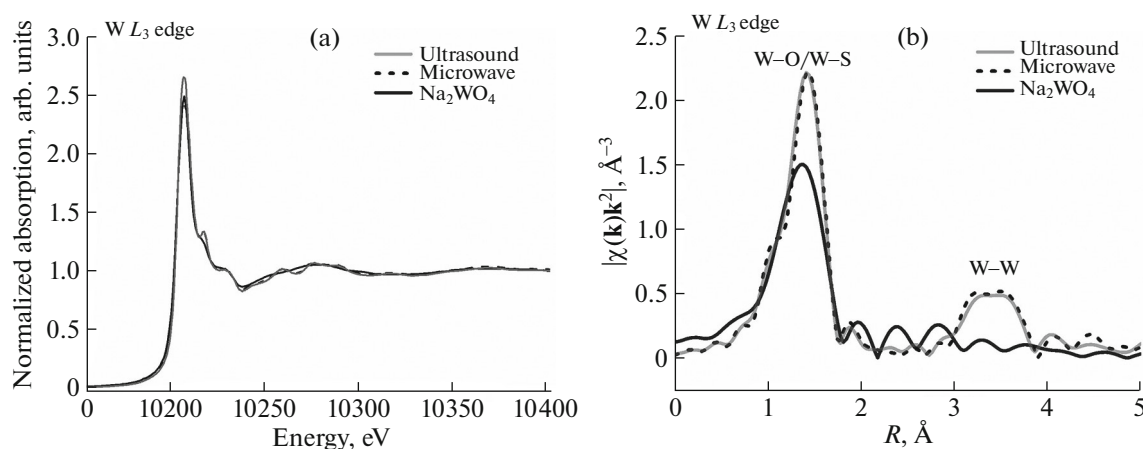


Fig. 3. X-ray absorption spectra obtained beyond the $W L_3$ edge for the initial precursor Na_2WO_4 and the tungsten complexes prepared by the microwave and ultrasonic methods: (a) is near-threshold fine structure of the X-ray absorption spectrum (XANES region); (b) is extended fine structure of the X-ray absorption spectrum (EXAFS).

The resulting normalized XANES spectra beyond the $W L_3$ edge are shown in Fig. 3a. It can be seen that the local environment in the vicinity of tungsten atoms in the complexes synthesized by the microwave and ultrasonic methods is identical. The higher intensity of the main absorption maximum (the so-called white line) observed for the sample obtained by ultrasonic synthesis may be associated with a slightly higher density of free states on the d - or p - d hybridized tungsten shells. Figure 3b shows the magnitudes of the amplitudes of the EXAFS signal obtained by the Fourier transform of the k^2 -weighted $\chi(k)$ oscillating function for complexes obtained by the ultrasonic- and microwave-synthesis methods. The main peak with a maxi-

um localized at 1.4 Å can be interpreted by the single scattering paths of W–O and W–S in the first coordination sphere of tungsten. A slight shoulder on the left side of the main peak may indicate slight differences in the lengths of the W–O and W–S bonds. The second pronounced feature in the EXAFS amplitudes has a maximum in the region of 3.4 Å, which can be uniquely associated with the intense contributions of single W–W scattering paths. However, we note that the shape of the second maximum of EXAFS amplitudes also indicates the presence of at least two possible W–W bond lengths differing within the range of 0.10–0.15 Å. In general, qualitative analysis of the extended region of X-ray absorption spectra (EXAFS region) indicates a high degree of identity of the local environment of tungsten atoms in complexes synthesized by the microwave and ultrasonic methods.

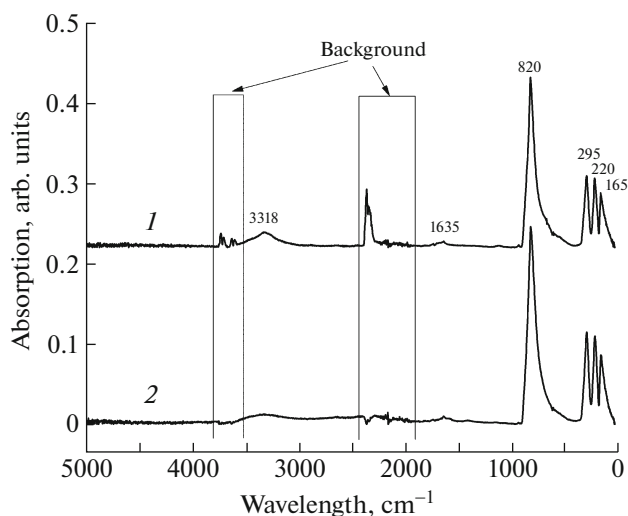


Fig. 4. IR spectra of the unithiol–tungsten complex samples: 1 is the ultrasonic sample; 2 is the microwave sample.

IR spectroscopy. To identify tungsten–unithiol complexes obtained by ultrasonic and microwave synthesis, the IR absorption spectra were measured in the range of 5000–0 cm^{-1} . The graphs are presented in Fig. 4. Peaks in the regions 3750–3550 and 2400–2100 cm^{-1} are background peaks and will not be considered.

The peaks at wavenumbers 220 and 295 cm^{-1} are likely due to coordination of the $W_2O_3^{4+}$ group through the tungsten–sulfur single bond. We note that the S–H bond vibrations observed in unithiol were not detected at the expected wavenumber of 2551 cm^{-1} , which indicates a fundamentally different structure of the complex with tungsten relative to pure unithiol. The peak at 820 cm^{-1} , broadened in the low-frequency region, presumably corresponds to vibrations of the W=O and W–O–W bonds in the $(O=W-O-W=O)^{4+}$ group, but

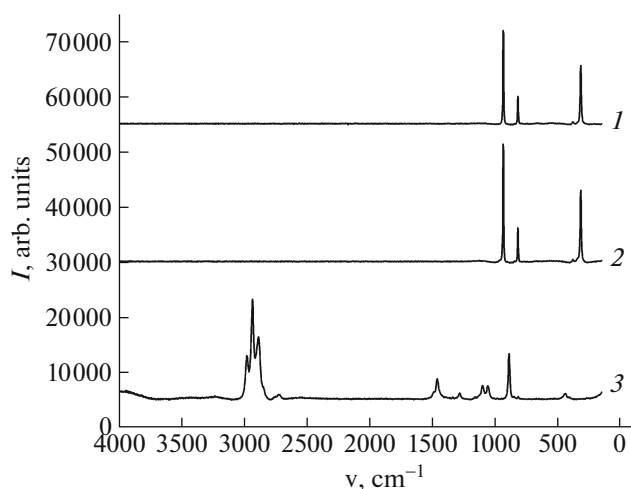


Fig. 5. Raman spectroscopy of the unithiol–tungsten complex samples: 1 is the ultrasonic sample; 2 is the microwave sample; 3 is the initial extract of *Picea pungens* Engelm. spruce.

there is almost no peak corresponding to the vibration of the W–O bond at 500 cm^{-1} , which may indicate incorrect interpretation of the value of this peak in [6], since according to X-ray diffraction a structure similar to that described in this work was obtained. The broadening of the peak at $3500\text{--}3100\text{ cm}^{-1}$ indicates the presence of water molecules of different nature in the complex and reconfirms the individuality of the structure of the tungsten–unithiol complex in comparison with unithiol, the IR spectrum of which shows peaks associated with the absorption of water in the lower frequency region at $3600\text{--}3400\text{ cm}^{-1}$. A very weak peak at a wavenumber of 1635 cm^{-1} indicates deformation vibrations of water in the complex and is located in a higher frequency region compared to the position of

this vibration at 1606 cm^{-1} in dihydrated unithiol according to data from [6].

In addition, a peak was found at 165 cm^{-1} comparable in intensity to the peaks at 220 and 295 cm^{-1} , but its exact nature is unknown.

Raman spectroscopy. For the first time, graphs of the Raman-scattering shift for the tungsten–unithiol complex were recorded on a EnSpectr R532 spectrometer (EnSpectr, Russia). The measurement results are presented in Fig. 5.

Transmission electron microscopy. Images of the powders were taken on a transmission electron microscope (TEM) G2 Spirit BioTWIN (FEI Company, the United States) and are shown in Fig. 6. In the ultrasonic sample, the particle size is $\sim 1000\text{ nm}$, they are covered with a layer of $\sim 100\text{-nm}$ particles that form a surface irregularity on individual crystallites, while some of them are rod shaped. In the TEM images of the microwave sample, the cubic shape of the grains with dimensions of $\sim 500\text{ nm}$ is visible.

CONCLUSIONS

It has been found that an ethanolic extract of blue spruce can be used as a source of unithiol to form a complex with metals, in particular with tungsten. This tungsten–unithiol complex was first synthesized by ultrasonic and microwave methods using natural raw materials as a source of unithiol. The synthesis method affects the particle size and morphology.

The resulting complex has high chemical resistance to widely used organic solvents, such as diethyl ether, benzene, toluene, ethyl alcohol, and carbon tetrachloride, but is soluble in water.

Antibacterial and fungicidal properties are proposed based on the data on biological activity with other heavy metals [6].

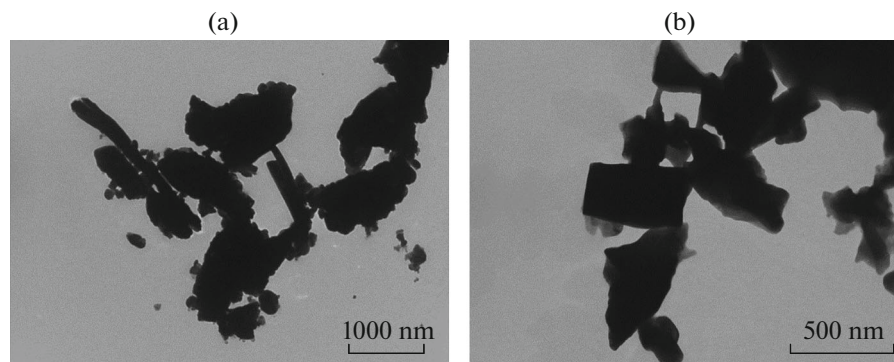


Fig. 6. TEM images of the unithiol–tungsten complex samples: (a) ultrasonic sample; (b) microwave sample.

FUNDING

The study was carried out with financial support from the Ministry of Science and Higher Education of the Russian Federation within the framework of the state assignment in the field of scientific activity no. FENW-2023-0019.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

REFERENCES

1. A. P. Arnold, A. J. Canty, P. W. Moors, and G. B. Deacon, *J. Inorg. Biochem.* **19**, 319 (1983).
[https://doi.org/10.1016/0162-0134\(83\)80005-1](https://doi.org/10.1016/0162-0134(83)80005-1)
2. E. Z. Jahromi, J. Gailer, I. J. Pickering, and N. G. Graham, *J. Inorg. Biochem.* **136**, 99 (2014).
<https://doi.org/10.1016/j.jinorgbio.2013.10.025>
3. F. W. Santos, J. B. T. Rocha, and C. W. Nogueira, *Toxicol. In Vitro* **20**, 317 (2006).
<https://doi.org/10.1016/j.tiv.2005.08.006>
4. P. A. M. Williams and E. J. Baran, *J. Inorg. Biochem.* **102**, 1195 (2008).
<https://doi.org/10.1016/j.jinorgbio.2007.12.006>
5. L. J. Anghileri, M. Ottaviani, S. Ricard, and C. Raynaud, *Eur. J. Nucl. Med.* **6**, 403 (1981).
<https://doi.org/10.1007/BF00266430>
6. A. K. Ospanova, Kh. K. Ospanov, G. Kh. Shabikova, et al., *Zh. Neorg. Khim.*, No. 1, 71 (1989).
7. A. A. Chernyshov, A. A. Veligzhanin, and Yu. V. Zubavichus, *Nucl. Instrum. Methods Phys. Res., Sec. A* **603**, 95 (2009).
<https://doi.org/10.1016/j.nima.2008.12.167>
8. B. Ravel and M. Newville, *J. Synchrotron Radiat* **12**, 537 (2005).

Translated by G. Levit

Publisher’s Note. Pleiades Publishing remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.