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SYNTHESIS, STRUCTURE, AND SPECTRAL STUDIES OF THE $(Et_4N)_4[Nb_2O_2(C_2O_4)_4(\mu\text{-}C_2O_4)]$ COMPLEX

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The bis(oxalate) complex of niobium $(NH_4)[NbO(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$ can be dissolved in DMF on heating. Ether diffusion into this solution in the presence of Et_4NBr leads to the formation of colorless crystals of $(Et_4N)_4[Nb_2O_2(C_2O_4)_4(\mu\text{-}C_2O_4)]$ (**1**). The characterization of the obtained compound by single crystal and powder XRD, IR and Raman spectroscopy, and elemental analysis allows to clarify processes occurring with the bis(oxalate) niobium complex in aqueous solutions.

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INTRODUCTION

Chemistry of Nb^V in aqueous solutions with pH < 7, which is necessary to obtain mixed polyoxometalates (POMs), is very limited, and it is the main distinction of chemistry with vanadium, niobium, and tantalum. Niobium complexes with organic ligands or niobium peroxocomplexes can be used as a source of niobium introduced into POMs. In the works of the early 20th century, water-soluble niobium and tantalum compounds with tartaric and citric acids were described and their composition was determined from the elemental analysis data [1-3]. There are many articles on niobium and tantalum complexes with an oxalate anion, but only the structures of compounds with niobium have been determined [4]. Both Nb^{IV} and Nb^V form oxalate complexes. The structures of the following oxalate Nb^{IV} complexes have been reported: $K_4[Nb(C_2O_4)_4]\cdot 3H_2O$, $K_2(H_3NCH_2CH_2)_2[Nb(C_2O_4)_4]\cdot 4H_2O$, and $K_4[Nb(C_2O_4)_4]\cdot 4H_2O\cdot 1/2H_2C_2O_4$ [5]. Nb^V typically forms tris(oxalato)oxoniobate(V) $[NbO(C_2O_4)_3]^{3-}$ [6-8], however, a commercially available product is a complex with two coordinated oxalate ligands $(NH_4)[NbO(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$ [4]. In an aqueous solution, $[NbO(C_2O_4)_2(H_2O)_2]^-$ is in equilibrium with the tris(oxalate) $[NbO(C_2O_4)_3]^{3-}$ complex [9]. We obtained $[NbO(C_2O_4)_3]^{3-}$ salts with protonated N-heterocyclic cations by adding stoichiometric amounts of bipyridine, phenanthroline, or aminopyridine in an aqueous solution of $(NH_4)[NbO(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$. The addition of organic cations shifts this equilibrium toward the formation of $[NbO(C_2O_4)_3]^{3-}$ due to a poor solubility of salts with protonated N-heterocyclic cations. The crystal structures of $(bpyH_2)(bpyH)[NbO(C_2O_4)_3]\cdot 2H_2O$, $(phenH)_3[NbO(C_2O_4)_3]\cdot 3H_2O$, and $(2\text{-}NH_2\text{-}pyH)_3[NbO(C_2O_4)_3]\cdot 2H_2O$ salts were determined by single crystal XRD [10]. The Raman spectroscopy data from the study by J.-M. Jehng and I.E. Wachs revealed the presence of binuclear forms $[NbO(C_2O_4)(H_2O)(\mu\text{-}O)_2NbO(C_2O_4)(H_2O)]^{2-}$ during the solvolysis of

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$(NH_4)[NbO(C_2O_4)_2(H_2O)_2]$ [9]. However, the structure of these as well as other solvation products has not yet been determined. In this work, we found the formation of the binuclear $[Nb_2O_2(C_2O_4)_4(\mu\text{-}C_2O_4)]^{4-}$ complex in a $[NbO(C_2O_4)_2(H_2O)_2]^-$ solution in DMF.

EXPERIMENTAL

Initial reagents were used without additional purification. The IR spectra were recorded using a diamond accessory on a FT-801 spectrometer (Simex, Russia). The elemental analysis was performed on Eurovector 3000. The Raman spectra were measured on a Triplemate spectrometer (Spex, USA) equipped with a multi-channel LN-1340 PB detector (Princeton Instruments, USA). A TG209 F3 Iris®NETZSCH derivatograph was used for the thermogravimetric analysis (TGA).

Synthesis of $(Et_4N)_4[Nb_2O_2(C_2O_4)_4(\mu\text{-}C_2O_4)]$ (1). 0.1 g (0.25 mmol) of $(NH_4)[NbO(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$ were dissolved on heating in 5 mL of DMF, then 0.214 mg (1.0 mmol) of Et_4NBr were added to the hot solution; after that the reaction mixture turned yellow. The mixture was stirred at 100 °C for 30 min and then cooled to room temperature. The colorless crystalline product was obtained by slow diffusion of diethyl ether vapor into the reaction mixture at 5 °C. Yield was 0.70 g (48% for $(NH_4)[NbO(C_2O_4)_2(H_2O)_2]$). IR (ν, cm^{-1}): 3942 (w), 3788 (w), 3585 (w), 3088 (w), 2989 (w), 1709 (vs), 1686 (vs), 1641 (vs), 1479 (m), 1461 (m), 1441 (m), 1395 (m), 1352 (vs), 1310 (s), 1221 (s), 1209 (m), 1174 (s), 1055 (w), 1001 (m), 932 (s), 906 (m), 884 (m), 847 (w), 809 (s), 783 (vs), 634 (w), 556 (s). Raman scattering (ν, cm^{-1}): 1464 (s), 1408 (w), 1390 (m), 1373 (m), 1357 (m), 1301 (m), 1222 (m), 1210 (m), 1173 (w), 1119 (m), 1068 (m), 1025 (w), 1003 (m), 940 (s), 920 (m), 906 (m), 793 (w), 677 (m), 661 (m), 565 (m), 541 (m), 520 (m), 470 (w), 419 (s), 354 (w), 337 (w), 303 (s), 294 (s), 283 (s), 273 (s), 262 (s), 100 (s). From the elemental analysis for $C_{42}H_{80}N_4Nb_2O_{22}$ calculated C, H, N (%): 42.8, 6.8, 4.8; found: 42.8, 6.8, 4.8.

Single crystal XRD. The structure of compound **1** was determined according to the standard procedure on an Xcalibur (Agilent Technologies) diffractometer at 130 K (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator). Reflection intensities were measured by φ-scanning of narrow (0.5°) frames. Absorption correction was applied empirically by the SCALE3 ABSPACK algorithm (CrysAlis PRO 1.171.38.41 (Rigaku OD, 2015)). The structure was solved using SHELXT [11] and refined by full-matrix LSM in the anisotropic approximation for non-hydrogen atoms using the SHELXL 2017\1 algorithm [12] in ShelXle [13]. Hydrogen atoms were refined in the geometrically calculated positions. Crystallographic data and refinement results for the structure of **1** are given in Table 1.

Atomic coordinates and other structural parameters for **1** have been deposited with the Cambridge Structural Database (No. 1877867; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Slow diffusion of ether into the DMF solution of $(NH_4)[NbO(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$ in the presence of tetraethylammonium bromide causes the growth of colorless $(Et_4N)_4[Nb_2O_2(C_2O_4)_4(\mu\text{-}C_2O_4)]$ crystals (**1**), which were isolated and characterized by single crystal and powder XRD.

The crystal structure of compound **1** contains tetraethylammonium cations and binuclear $[Nb_2O_2(C_2O_4)_4(\mu\text{-}C_2O_4)]^{4-}$ anions (Fig. 1). Each complex anion consists of two $\{NbO(C_2O_4)_2\}^-$ moieties linked by a bridging oxalate ligand (*d*(Nb1–O5) = 2.3093(13) Å; *d*(Nb1–O6) = 2.1766(13) Å). In each such moiety the niobium atom has CN 7: the terminal oxo ligand (*d*(Nb1–O11) = 1.7047(14) Å) and six oxygen atoms from asymmetrically coordinated oxalate ligands. For equatorial oxalate ligands the Nb–O bond lengths vary from 2.0804(14) Å to 2.1207(14) Å. The coordination polyhedron of the niobium atom is a slightly distorted pentagonal bipyramid in the $[NbO(C_2O_4)_2(H_2O)_2]^-$ and $[NbO(C_2O_4)_3]^{3-}$ anions. At the base of the pyramid, there are four oxygen atoms from oxalate ligands and one oxygen atom of a water molecule in the case of the first anion and five oxygen atoms from oxalate ligands in the case of the second anion. In the structure of $[Nb_2O_2(C_2O_4)_4(\mu\text{-}C_2O_4)]^{4-}$ one of the equatorial ligands is strongly bent (Fig. 2) due to $O\ldots H_3C$ contacts, with O2 and O3 forming the shortest contacts (*d*(O…C) = 3.133 Å and 3.263 Å).

TABLE 1. Crystallographic Characteristics and Details of the Diffraction Experiment for Compound **1**

Parameter	Value
Chemical formula	$C_{42}H_{80}N_4Nb_2O_{22}$
M	1178.92
Crystal symmetry	Monoclinic
Space group	$C2/c$
a, Å	26.3491(15)
b, Å	13.3584(8)
c, Å	14.9018(7)
β, deg	92.421(5)
V, Å^3	5240.5(5)
Z	4
ρ(calc.), g/cm^3	1.494
μ, mm^{-1}	0.52
F(000)	2472
Crystal size, mm	0.25×0.25×0.20
θ range of data collection, deg	3.3-29.6
Intervals of reflection indices	$-35 \le h \le 33$, $-18 \le k \le 18$, $-20 \le l \le 20$
Measured reflections	14303
Independent reflections (R_{int})	6220 (0.022)
Reflections with $I > 2\sigma(I)$	5220
Refined parameters	318
$GOOF$	1.04
R_1 ($I > 2\sigma(I)$)	0.031
wR_2 (all reflections)	0.074
$\Delta\rho_{min}$ / $\Delta\rho_{max}$, e/Å^3	–0.50 / 0.56

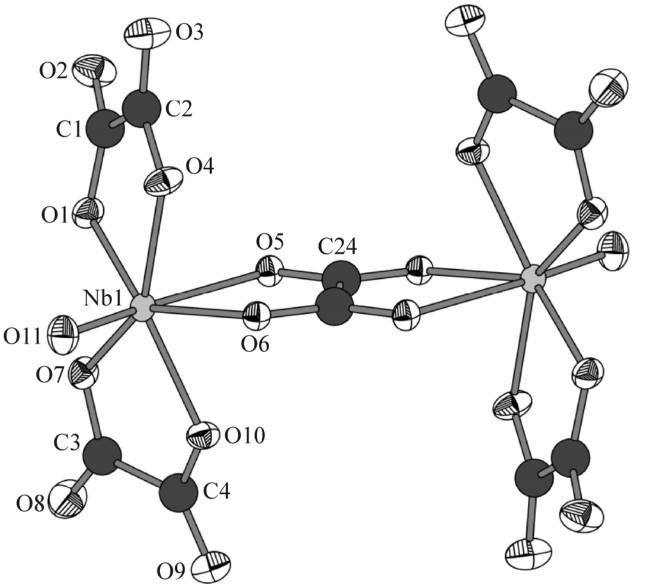

Fig. 1. Structure of the $[Nb_2O_2(C_2O_4)_4(\mu\text{-}C_2O_4)]^{4-}$ anion in complex **1**.

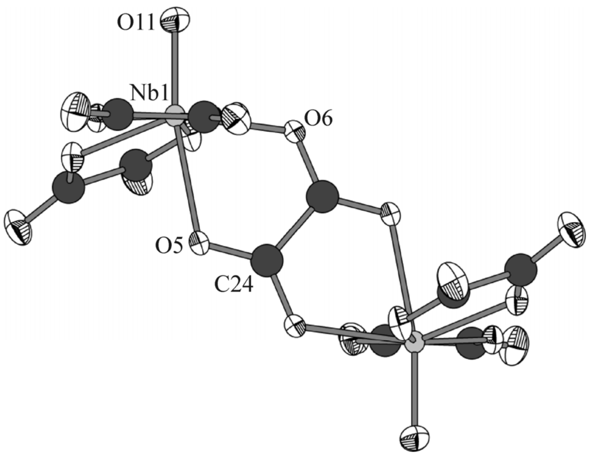

Fig. 2. Distortion of the Nb1 coordination polyhedron in the structure of complex **1**.

In the crystal structures of $(bpyH_2)(bpyH)[NbO(C_2O_4)_3]\cdot 2H_2O$, $(phenH)_3[NbO(C_2O_4)_3]\cdot 3H_2O$, and $(2\text{-}NH_2\text{-}pyH)_3[NbO(C_2O_4)_3]\cdot 2H_2O$ complexes the coordination environment (CN 7) of the Nb atom in $[NbO(C_2O_4)_3]^{3-}$ is pentagonal bipyramidal and includes three asymmetrically coordinated oxalate ligands (d(Nb–O) = 2.110(2)-2.206(2) Å) and the terminal oxo ligand (d(Nb=O) = 1.719(2)-1.730(2) Å). Thus, for compound **1** all Nb–O distances are shorter, apparently, due to weakening of intermolecular interactions.

In the crystal structure $[Nb_2O_2(C_2O_4)_4(\mu\text{-}C_2O_4)]^{4-}$ anions form pseudo-layers oriented in the [110] plane (Fig. 3).

It is noteworthy that on dissolving $(NH_4)[NbO(C_2O_4)_2(H_2O)_2]$ in DMF, a series of chemical reactions are most likely to undergo, perhaps, with substitution of the oxalate ligand in the niobium coordination sphere. Since complex **1** isolated by crystallization contains five oxalate anions per two Nb, it is reasonable to assume the presence of mononuclear $[NbO(C_2O_4)(DMF)_x(H_2O)_{4-x}]^+$ or more complex forms in the reaction mixture. Unfortunately, attempts to crystallize these products have not yet led to positive results.

Previously, the behavior of $(NH_4)[NbO(C_2O_4)_2(H_2O)_2]$ in an aqueous solution was studied by IR and Raman spectroscopy [9, 14]. It was shown that when pH increased, the solvation of the complex occurs with a detachment of the oxalate ligands and the formation of $[NbO(C_2O_4)(H_2O)(\mu\text{-}O)_2NbO(C_2O_4)(H_2O)]^{2-}$. However, the authors traced this by an increase in the Raman band intensity at 520 cm^{-1}, which was attributed to Nb–O–Nb vibrations. In the IR spectrum, the vibrational bands at 890 cm^{-1} and 630 cm^{-1} were assigned to the dimer, although in the Raman spectrum of complex **1** this 520 cm^{-1} band is also present (Fig. 4). According to the powder XRD and elemental analysis data, complex **1** does not contain by-products. Hence, it is possible to question the correctness of this band assignment. Note that the bands at 884 cm^{-1} and 634 cm^{-1} are present in the IR spectrum of **1**. This implies that during the solvolysis of $[NbO(C_2O_4)_2(H_2O)_2]^-$ the $[Nb_2O_2(C_2O_4)_4(\mu\text{-}C_2O_4)]^{4-}$ dimers can form due to the appearance of a free oxalate anion in the system. The French chemists described in the literature complexes with the composition $((C_2H_5)_4N)_2[Nb_2^VO_2X_6(C_2O_4)]$ (X = Cl, Br), where the bridging arrangement of the oxalate anion is assumed [15]. Unfortunately, their structures have never been determined, although there are data on the presence of a 474 cm^{-1} band in the IR spectrum, which is assigned to the vibration of the bridging oxalate ligand. In the IR spectrum of compound **1** this band is poorly distinguishable; in the Raman spectrum it is weak at 470 cm^{-1}. The Nb=O vibrations have the highest intensity in the Raman spectrum (940 cm^{-1} band) and a medium intensity in the IR spectrum (932 cm^{-1} band). In the $(H_3O)_2[Nb^{IV}{}_2O_2C1_6]$ complex the Nb=O vibrational band in the IR spectrum remains at 930 cm^{-1} despite a change in the Nb oxidation state [16].

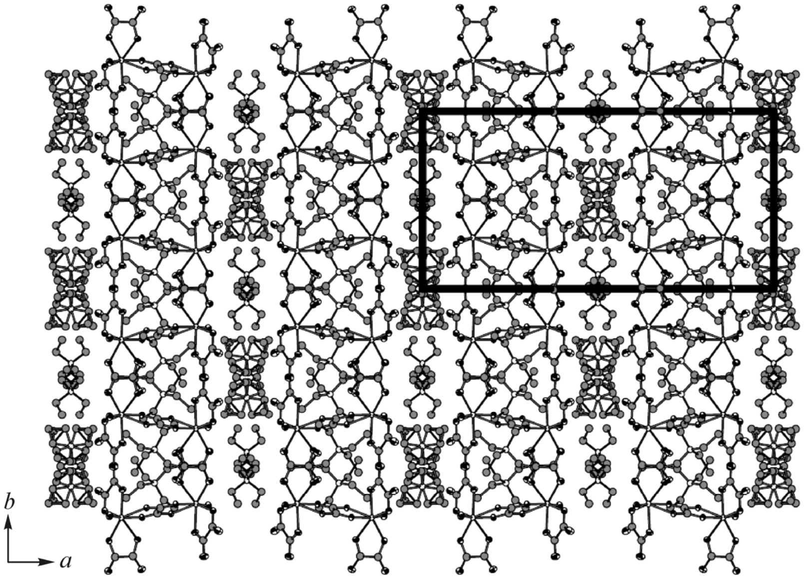

Fig. 3. Crystal packing of complex **1** (view along the *c* crystallographic axis).

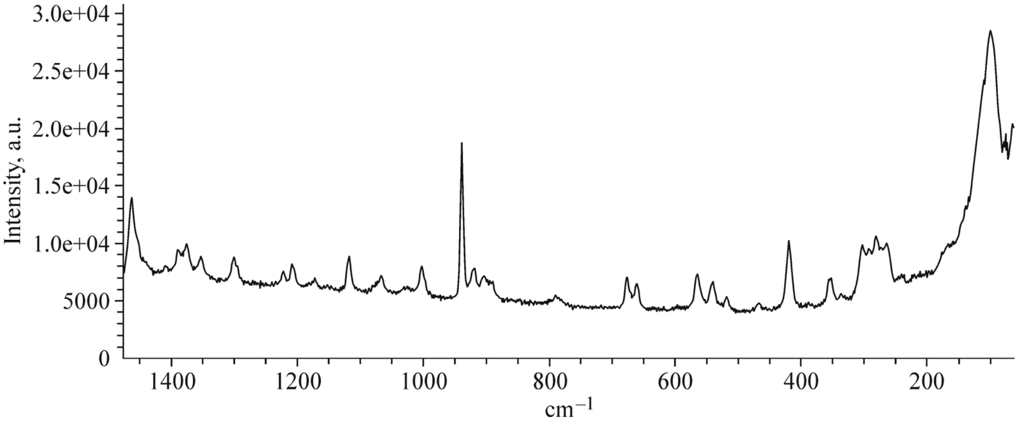

Fig. 4. Raman spectrum of complex **1** in the solid phase.

Thus, the isolation of the binuclear $(Et_4N)_4[Nb_2O_2(C_2O_4)_4(\mu\text{-}C_2O_4)]$ complex allowed us to bring some clarity in a complex solvation process of the mononuclear oxalate niobium complex in an aqueous solution. Unfortunately, the solubility of compound **1** in organic solvents is very low, which currently hinders the study of its coordination chemistry. The research in this field is ongoing.

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CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

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