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The crystal structure of μ -Oxo-bis{diethoxy[salicylaloximato(2-)]-tantalum(V)}

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ABSTRACT

Stoichiometric reaction of salicylaldoxime and tantalum or niobium ethoxide in toluene at room temperature resulted in formation of $[M_2O(C_7H_5NO_2)_2(C_2H_5O)_4]$, M=Ta and Nb which were crystallized from CH_2Cl_2 at $-5^\circ C$ and characterized by spectroscopic techniques. The molecular structures of $[Ta_2O(C_7H_5NO_2)_2(C_2H_5O)_4]$ was determined by single-crystal X-ray diffraction and compared with molecular structure of $[Nb_2O(C_7H_5NO_2)_2(C_2H_5O)_4]$. The geometries at metal atoms are distorted octahedron which shared an apex through bridged oxygen. Each dianionic salicylaldoximate ligand chelates to the one metal ion through its phenolic oxygen and oximate oxygen atom, and to another metal ion through its oximate nitrogen atom.

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1. Introduction

Metal oxo-bridged alkoxides are important intermediates of oligomeric metal alkoxides and metal oxides and they can be products of controlled hydrolysis of metal alkoxide or side product in preparation of metal alkoxides from metal oxide. They are also produced by ether elimination from metal alkoxides or reaction of metal oxo-chlorides with alkali alkoxides [1]. Although their hydrolytic stability increases with oxo content [2], they are still reactive toward water or alcohol exchange processes and stabilizing them with chelating ligands is subject of interest and desire in sol-gel processing. Numbers of chelating ligands have been used for the stabilization of metal oxo-bridged alkoxides, such as polyols [3], carboxylates [4,5], β -diketonates [6] and alkanolamines [7] and a variety of their derivatives have been isolated. Interestingly, the stabilized metal alkoxides show different behavior in the hydrolysis-condensation process and that reflects in

the properties of final materials [8]. This approach has been used in industry for tailoring metal oxides with well-defined specification for the fabrication of advanced ceramics. Evidently, the stability of modified metal oxo-alkoxides depends on the type of ligands and coordination status of them. Apparently, hydrolytic stability of metal alkoxides increases by decreasing the number of alkoxy groups, and consequently their alkoxy character vanishes, in which their hydrolysis requires harsh media [2]. Recent studies show that, due to the lability of metal oxo-alkoxides, alkoxy groups quite readily can be replaced by a wide variety of ligands containing hydroxyl group [9–11]. Over the last decade, several efforts have been conducted to elucidation of coordination chemistry of salicylaldoxime and its derivatives due to the ability of the dianions of those ligands to produce high nuclearity metal complexes [12]. Salicylaldoxime (2-hydroxybenzaldehyde oxime), which is a primitive member of phenolic oxime ligands, has been mentioned in a 1964 edition of Vogel's textbook of inorganic analysis as an inorganic reagent. This ligand chelates to metal ion through the phenolic oxygen and oximate nitrogen atoms in mono-deprotonated form. Interestingly, the free OH oxime group of complex usually

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engages in hydrogen bonding with water molecules or phenolic oxygen atoms of neighboring salicylaldehyde ligands [13,14] or other molecules [15] to stabilize structure. In the mono-deprotonated form, 2-hydroxybenzaldehyde oxime usually produces mono- or bi-nuclear complexes, which are used in separation analysis, metal extraction and nano-crystal preparation [16]. In a doubly-deprotonated anion, salicylaldehyde usually uses its phenolic oxygen and oximate nitrogen atoms to chelate to one metal ion and its oximate oxygen as bridging unit to bonds to neighboring metal ion, so it can produce poly-nuclear complexes in this form. These poly-nuclear complexes are relevant to several areas of science and technology, including corrosion inhibition [17]. To the best of our knowledge, there is a limited number of structurally characterized doubly-deprotonated salicylaldehyde of alkoxide complexes [10,18,19] and this is the first report on tantalum alkoxide complexes with salicylaldehyde. During the course of stabilization of metal alkoxides for the fabrication of metal oxides and in the interest in how structural modification would alter the final texture of metal oxides, we have prepared salicylaldehyde derivatives of tantalum and niobium alkoxides. Herein, we report synthesis and characterization of two dinuclear complexes of Ta(V) and Nb(V) with salicylaldehyde, $[M_2O(C_7H_5NO_2)_2(C_2H_5O)_4]$, M=Ta (**I**) and Nb (**II**). These complexes were characterized by 1H , ^{93}Nb -NMR, UV-Vis and Mass spectrometry, in addition to the single-crystal structure of **II** in light of our previous study [9].

2. Materials and methods

All manipulations were carried out under nitrogen, using standard Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. Salicylaldehyde [20], niobium(V) pentaethoxide and tantalum(V) pentaethoxide [1] were prepared according to the reported procedures. IR spectra were recorded on a Shimadzu 470 instrument at 4 cm^{-1} resolution, using KBr pellets. The 1H and ^{93}Nb -NMR spectra were obtained in $CDCl_3$ using a Bruker DRX-500 spectrometer. The mass spectrometry was performed on a Varian Matt 44 instrument (electron impact, 20 eV). UV-Vis spectra were recorded on a Shimadzu 2100 spectrophotometer.

3. Experimental

3.1. Preparation of metalorganic compounds

3.1.1. $[Ta_2O(C_7H_5NO_2)_2(C_2H_5O)_4]$ (**I**)

Compound **I** was prepared by reaction of salicylaldehyde (0.55 g, 4 mmol) with $Ta(OCH_2CH_3)_5$ (1.62 g, 4 mmol) in toluene (10 mL). The mixture was stirred for a day and the solvent then was removed under reduced pressure to furnish a yellowish solid. The solid was crystallized from dichloromethane-ether. Suitable crystals of complex for single-crystal structure determination were isolated from solution after several days at $-5\text{ }^\circ\text{C}$ (m.p., decomposed at $270\text{ }^\circ\text{C}$). Anal. Calcd. for $C_{22}H_{30}N_2O_9Ta_2$: C, 31.88; H, 3.62; N, 3.38%. Found: C, 32.06; H, 3.84; N, 3.23%. UV (CH_2Cl_2 , nm): 246 (LMCT), 280 (π to π^*), 345 (n to π^*). IR (cm^{-1}): 3058 (C-H, aromatic), 2920 (C-H, aliphatic), 1600 (C=N),

1556 (C=C), 1287 (C-O), 670 (Ta-O-C, symmetric), 577 (Ta-O-C, asymmetric). 1H -NMR ($CDCl_3$, ppm): 1.02 (6H, t, CH_3), 1.46 (6H, t, $-CH_3$), 4.21 (4H, q, $-OCH_2-$), 4.81 (4H, q, $-OCH_2-$), $C_7H_5NO_2$ ligand protons: 6.90 (4H, m), 7.12 (2H, m), 7.37 (2H, m), 8.14 (2H, s, $CH=N$).

3.1.2. $[Nb_2O(C_7H_5NO_2)_2(C_2H_5O)_4]$ (**II**)

Compound **II** was prepared, according to the earlier report [9], by reacting salicylaldehyde (0.55 g, 4 mmol) to $Nb(OCH_2CH_3)_5$ (1.27 g, 4 mmol) in toluene (10 mL). The mixture was stirred for a day and the solvent then was removed under reduced pressure to furnish an orange solid. The solid was crystallized from dichloromethane/hexane; crystals of complex were isolated from solution after several days at $-5\text{ }^\circ\text{C}$. (m.p., decomposed at $250\text{ }^\circ\text{C}$). Anal. Calcd. for $C_{22}H_{30}N_2O_9Nb_2$: C, 40.49; H, 4.60; N, 4.29%. Found: C, 40.86; H, 4.72; N, 4.16%. UV (CH_2Cl_2 , nm): 231 (LMCT), 277 (π to π^*), 357 (n to π^*). IR (cm^{-1}): 3045 (C-H, aromatic), 2905 (C-H, aliphatic), 1592 (C=N), 1553 (C=C), 1278 (C-O), 671 (Nb-O-C, symmetric), 579 (Nb-O-C, asymmetric). 1H -NMR ($CDCl_3$, ppm): 1.16 (6H, t, CH_3), 1.45 (6H, t, $-CH_3$), 4.47 (4H, q, $-OCH_2-$), 4.62 (4H, q, $-OCH_2-$), $C_7H_5NO_2$ ligand protons: 6.88 (4H, m), 7.09 (2H, dd), 7.30 (2H, dt), 7.94 (2H, s, $CH=N$). ^{93}Nb -NMR ($CDCl_3$, ppm): 132 (6 coordinated Nb atom, referenced to $NbCl_6^-$). Mass spectrum data, niobium bearing fragments (m/e): 652 $[Nb_2O(OCH_2CH_3)_4(C_7H_5NO_2)_2]^+$, 607 $[Nb_2O(OCH_2CH_3)_3(C_7H_5NO_2)_2]^+$, 562 $[Nb_2O(OCH_2CH_3)_2(C_7H_5NO_2)_2]^+$, 547 $[Nb_2O(OCH_2CH_3)(OCH_2)(C_7H_5NO_2)_2]^+$, 517 $[Nb_2O(OCH_2CH_3)(C_7H_5NO_2)_2]^+$, 502 $[Nb_2O(OCH_2)(C_7H_5NO_2)_2]^+$, 489 $[Nb_2O(OH)(C_7H_5NO_2)_2]^+$. Mass numbers are based upon 1H , ^{12}C , ^{14}N , ^{16}O , and ^{93}Nb .

3.2. Crystal structure determination and refinement

A crystal of $0.20 \times 0.13 \times 0.10\text{ mm}^3$ of **I** was removed from its liquor and mounted on a fiber glass. The diffraction measurements were conducted on a STOE IPDS-II diffractometer with graphite monochromated $Mo\ K\alpha$ radiation, using the STOE X-AREA software package [21]. Cell constants and an orientation matrix for the data collection were obtained by least-squares refinement of diffraction data from 6917 unique reflections for **I**. Data were collected at 298 K to a maximum 2θ value of 29.17° for **I** in a series of ω scans in 1° oscillations. Data were integrated using the Stoe X-AREA software package [21]. A numerical absorption correction was applied in each case using X-RED [22] and X-SHAPE [23] software. The structures were solved by methods and refined on F^2 using a full-matrix least-squares procedure with anisotropic displacement parameters [24]. Atomic factors were obtained from the International Tables for X-ray Crystallography (Kluwer Academic Publisher 1995). All refinements were performed using the X-STEP32 crystallographic software package [25]. Crystal data and refinement details are listed in Table 1. The highest peaks and deepest holes for this compound are around the Ta atom (a distance of 0.81 \AA for highest peak and 0.77 \AA for deepest hole).

An orange block shaped crystal of **II**, air stable at room temperature, was used for the crystallographic measurements and reported elsewhere [9].

Table 1
Crystal data and structure refinement for compound **I**.

Empirical formula	C ₂₂ H ₃₀ N ₂ O ₉ Ta ₂
Formula weight	828.38
Temperature	298 (2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell dimensions	
<i>a</i>	10.7212 (9) Å
<i>b</i>	12.1002 (11) Å
<i>c</i>	12.0268 (10) Å
α	63.323 (6)°
β	78.988 (7)°
γ	68.542 (7)°
Volume	1296.8 (2) Å ³
<i>Z</i>	2
Density (calculated)	2.122 mg/m ³
Crystal size	0.20 × 0.13 × 0.10
Theta range for data collection	1.90–29.17°
Index ranges	–14 ≤ <i>h</i> ≤ 14 –16 ≤ <i>k</i> ≤ 13 –16 ≤ <i>l</i> ≤ 16
Reflections collected	14593
Independent reflections	6917 [R(int) = 0.0712]
Max. and min. transmission	0.439 and 0.290
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	6917/0/316
Goodness-of-fit on F2	1.126
Final R indices for reflections with $I > 2\sigma(I)$	0.0435
R indices (all data)	0.0469

4. Results and discussion

4.1. Spectroscopic studies

4.1.1. Mass spectrometry

An attempt has been made to record mass spectra of **I** and **II**, however, we succeeded only to observe metal bearing fragments in mass spectrum of **II**. The formulation of **II** was readily established by observation of its parent ion in mass spectrometry which is quite rare in the mass spectrum of metal alkoxides. Observation of the parent's ion can be attributed to the stability of **II** and a drastic change in its alkoxide character. The absence of metal bearing fragments in mass spectrum of **I** cannot be attributed to its instability because the structures of **I** and **II** and their properties are almost similar. This may be attributed to the higher molecular weight and lower volatility of **I** in comparison with **II**.

4.1.2. NMR spectroscopy

The ¹H-NMR spectrum of **I** shows two triplets at $\delta = 1.02$ and 1.46 ppm and two quartets at $\delta = 4.21$ and 4.81 ppm which are assigned to methyl and methylene groups of ethoxide ligands respectively. The same features were observed for **II** in the ¹H-NMR spectrum with $\delta = 1.16$ and 1.45 ppm for methyl and at $\delta = 4.47$ and 4.62 ppm for methylene groups. These data showed that there is two un-equivalent ethoxides group in the both compounds. This was confirmed by single-crystal X-ray structure analysis. Both ¹⁸¹Ta (*I* = 7/2) and ⁹³Nb (*I* = 9/2) nuclei, with 99.99% and 100% natural abundances respectively, are potentially NMR active. Attempts have been made to

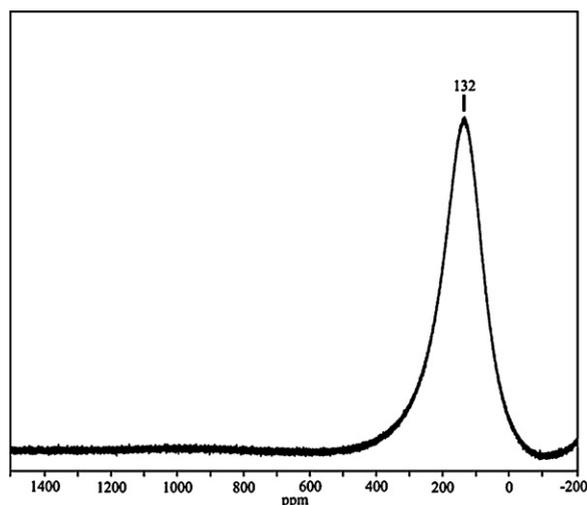


Fig. 1. ⁹³Nb NMR spectrum of **I**.

record ¹⁸¹Ta and ⁹³Nb-NMR spectra of **I** and **II**, respectively; however, because of the lower magnetogyric ratio and relative receptivity of the tantalum nucleus in comparison with the niobium nucleus we were succeeded only to record the ⁹³Nb-NMR spectrum [26]. The ⁹³Nb-NMR spectrum of **II** (Fig. 1) showed only a broad band centred at $\delta = 132$ ppm which is assigned to the presence of six coordinated niobium ions in solution [27] and this shows that the solid structure retains in solution. Since both compounds have a similar structure, retention of solid state structure in solution for **I** can also be concluded.

4.2. Crystal structures

Since the coordination mode of the salicylaldehyde group was ambiguous from spectroscopic data, both **I** and **II** (for comparison) were subject to single-crystal X-ray analysis. Perspective drawings of compound **I** is shown in Fig. 2. Crystallographic data and selected geometric parameters for compound **I** are given in Tables 1 and 2

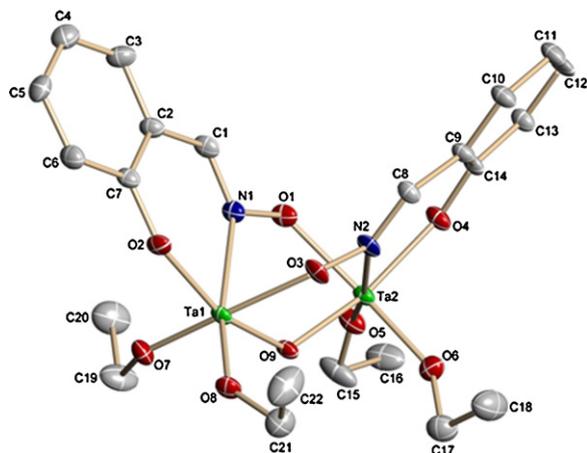


Fig. 2. The structure of **I**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

Table 2
Bond lengths [Å] and angles [°] for compound **I**.

Ta-N _{oxim}	Ta(1)-N(1)	2.296 (4)	Ta-μ-O _{oxo} -Ta O _{phenolic} -Ta-N _{oxim}	O(7)-Ta(1)-O(3)	169.10 (15)
	Ta(2)-N(2)	2.309 (4)		O(8)-Ta(1)-N(1)	165.20 (16)
Ta-O _{oxim}	Ta(1)-O(3)	2.055 (4)	O(9)-Ta(1)-O(2)	156.83 (14)	
	Ta(2)-O(1)	2.048 (4)	O(5)-Ta(2)-N(2)	170.42 (17)	
Ta-O _{phenolic}	Ta(1)-O(2)	1.955 (4)	O(6)-Ta(2)-O(1)	165.68 (15)	
	Ta(2)-O(4)	1.958 (3)	O(9)-Ta(2)-O(4)	156.58 (15)	
Ta-O _{oxo}	Ta(1)-O(9)	1.928 (3)	Ta(1)-O(9)-Ta(2)	128.00 (18)	
	Ta(2)-O(9)	1.920 (3)	O(2)-Ta(1)-N(1)	78.41 (14)	
Ta-O _{ethoxy}	Ta(1)-O(7)	1.880 (4)	O(4)-Ta(2)-N(2)	78.31 (14)	
	Ta(1)-O(8)	1.896 (4)			
	Ta(2)-O(5)	1.875 (4)			
	Ta(2)-O(6)	1.883 (4)			

respectively. Complexes **I** and **II** are iso-structure and crystallize in the triclinic space group $P\bar{1}$ with $Z = 2$ but the unit cell volume of **I**, 1296.8 Å³, somewhat is smaller than **II**, 1335.6 Å³. This requires longer unit cell dimensions of **II** in comparison with **I**. It can be seen that the geometry at niobium and tantalum atoms is similar. For both compounds, the geometry at the metal center is distorted octahedral which shared an apex through the bridged oxygen. Each dianionic salicylaldoximate ligand, chelates to the one metal through its phenolic oxygen and oximate nitrogen atoms, and to another metal through its oximate oxygen atom. One ethoxide at each metal centre is trans to oximate nitrogen and another one is trans to oximate oxygen. So, the latter one is above the phenyl ring and shielded by its anisotropic effect and appears at lower chemical shift in comparison with the former.

Apparently, the bond lengths of two metal ions in both compounds are similar to some extent. The longest bond lengths in **I** are Ta-N_{oxim}: 2.296 (4) and 2.309 (4) Å, which are comparable to Nb-N_{oxim} in **II**, 2.333 (2) and 2.337 (2) Å and Mo-N_{oxim} in [MoO(O₂)₂(OC₆H₄CH=NOH)], 2.374 (2) Å [28]. These are somewhat longer than V-N_{oxim} in [VO{ON=C(CH₃)(C₄H₃O-2)}₃], 1.969 (7)–2.287 (7) Å, [VO{ON=C(CH₃)(C₄H₃S-2)}₃].0.5C₆H₆, 1.991 (3)–2.196 (3) Å [29], [VOCl{ON=C(CH₃)(C₄H₃S-2)}₂].CH₃OH, 1.971 (5)–1.985 (5) Å [30], [VO(H₂O)(OC₆H₄C(O)NO)].1.58H₂O, 2.030 (3) Å, V₃O₃(H₂O)₃(OC₆H₃ClC(O)NO)₃.3CH₃COCH₃, 2.019 (3)–2.037 (3) Å [31], [V₃(μ₃-O)(OC₆H₄CH=NO)₂(OC₆H₄CH=NOH)(OC₆H₄CH(N=CHC₆H₄O)₂)₂], 2.098 (6)–2.135 (5) Å [32] and Mo-N_{oxim} in [(CH₃)₂CNO]Mo(C₅H₅)(CO)₂, 2.089 (12) Å [33]. But they are somewhat shorter than those reported for Mo-N_{oxim} in [Mo₄O₁₂{Me₂NHCH₂C(NH₂)NO]₂], 2.443 (3) Å, [Mo₄O₁₂{NC-CH=CH-C(NH₂)NO]₂]²⁻, 2.440 (3) Å [34] and W-N_{oxim} in [W₄O₁₂{MeC(NH₂)NO]₂]²⁻, 2.572 (33) and 2.578 (3) Å [35].

The next longest bond lengths in **I** are Ta-O_{oxim}: 2.048 (4) and 2.055 (4) Å, which are identical and comparable with Nb-O_{oxim} in **II**, 2.061 (1) and 2.071 (1) Å and V-O_{oxim} in [(η⁵-C₅H₄CH₃)₂V(ONC(CN)₂)₂], 2.0354 (9) Å [36]. These are also somewhat longer than V-O_{oxim} in [VO{ON=C(CH₃)(-C₄H₃O-2)}₃], 1.886 (6)–1.938 (6) Å, VO{ON=C(CH₃)(C₄H₃S-2)}₃.0.5C₆H₆, 1.908 (2)–1.935 (2) Å [29], [VOCl{ON=C(CH₃)(C₄H₃S-2)}₂].CH₃OH, 1.917 (4)–1.931 (4) Å [30], [VO(H₂O)(OC₆H₄C(O)NO)].1.58H₂O, 1.851 (3) Å, [V₃O₃(H₂O)₃(OC₆H₃ClC(O)NO)₃].3CH₃COCH₃, 1.852 (3)–1.861 (3) Å, [VO(HOC

H₄C(O)N(H)O)(C₅H₃N(C(O)O)₂], 1.850 (3) Å [31], [V₃(μ₃-O)(OC₆H₄CH=NO)₂(OC₆H₄CH=NOH)(OC₆H₄CH(N=CHC₆H₄O)₂)₂], 1.920 (5)–1.935 (5) Å [32] and Mo-O_{oxim} in [MoO(O₂)₂(OC₆H₄CH=NOH)], 1.983 (2) Å [28]. But they are somewhat shorter than those reported for Mo-O_{oxim} in [Mo₄O₁₂{Me₂NHCH₂C(NH₂)NO]₂], 2.179 (2) Å, [Mo₄O₁₂{NC-CH=CH-C(NH₂)NO]₂]²⁻, 2.188 (2) Å [34], and Mo-O_{oxim} in [(CH₃)₂CNO]Mo(C₅H₅)(CO)₂, 2.139 (12) Å [33] and for W-O_{oxim} in [W₄O₁₂{MeC(NH₂)NO]₂]²⁻, 2.200 (2) and 2.215 (2) Å [35].

The third longest bond lengths in **I** are Ta-O_{phenolic}: 1.955 (4) and 1.958 (3) Å. They are very close to Nb-O_{phenolic} in **II**, 1.969 (1) and 1.971 (1) Å and V-O_{phenolic} in [V₃(μ₃-O)(OC₆H₄CH=NO)₂(OC₆H₄CH=NOH)(OC₆H₄CH(N=CHC₆H₄O)₂)₂], 1.925 (4)–1.967 (5) Å [32]. These are somewhat shorter than Nb-O_{phenolic} in [Nb(C₉H₆NO)₃O].2CH₂Cl₂, 2.052 (2) and 2.054 (3) [10], [Nb(C₉H₆NO)(OEt)₄], 2.060 (5) [37] and Ta-O_{phenolic} in [Ta(C₉H₆NO)₃O].2CH₂Cl₂, 2.036 (2) and 2.049 (3) [11]. On the other hand, these are somewhat longer than those found for V-O_{phenolic} in [VO(H₂O)(OC₆H₄C(O)NO)].1.58H₂O, 1.868 (3) Å and [V₃O₃(H₂O)₃(OC₆H₃ClC(O)NO)₃].3CH₃COCH₃, 1.862 (2)–1.898 (3) Å [31].

Furthermore, the Ta-O_{oxo} bond lengths in **I**, 1.920 (3) and 1.928 (3) Å and Nb-O_{oxo} lengths in **II**, 1.930 (1) and 1.940 (1) Å are nearly identical. They are also comparable to metal oxo-bridge bond distances in the [(μ-CH₃C(CH₂O)₂C(O)O)Nb₂(μ-O)(OEt)₅]₂, 1.945 (5) and 1.911 (5) Å [4], [Nb₂O(O₂C₆H₁₂)₂(HO₂C₆H₁₂)₄], 1.929 (3) and 1.905 (2) Å and [Ta₂O(O₂C₆H₁₂)₂(HO₂C₆H₁₂)₄], 1.925 (5) and 1.919 (5) Å [38], Nb₆O₈(^tPrO)₁₄(^tPrOH)₂, 1.838 (9)–2.034 (9) Å [39], Nb₂O(O₂CCMe₃)₂(OCH₂CMe₃)₆, 1.960 (11) and 1.847 (12) Å, Ta₂O(O₂CCMe₃)₂(OCH₂CMe₃)₆, 1.899 (13) and 1.916 (14) Å, [Nb(O)(O₂CCH₂CMe₃)(OCH₂CMe₃)₂]₄, 1.801 (7)–2.032(8) Å, [Ta(O)(O₂CCMe₃)(OCH₂CMe₃)₂]₄, 1.841 (5)–2.079 (6) Å and Ta₄(O)₄(O₂CCH₂CMe₃)₄(OCH₂CMe₃)₈, 1.739 (10)–2.177 (11) Å [40], [Ta₈(μ₃-O)₂(μ-O)₈(μ-OEt)₆(OEt)₁₄], 1.838 (14)–2.038 (13) Å, [Ta₇(μ₃-O)₃(μ-O)₆(μ-OPr^t)₄(OPr^t)₁₃], 1.845 (12)–2.020 (11) Å, [Ta₅(μ₃-O)₄(μ-O)₃(μ-OBu^t)(OBu^t)₁₀], 1.819 (18)–2.026 (15) Å [41], Nb₆(μ-O)₃(μ-O₂CCF₃)₆(μ-OC₂H₅)₆(OC₂H₅)₆, 1.903 (4)–1.930 (4) Å [42], Nb₄O₄(O₂CCH₃)₄(OPr^t)₈, 1.86 (1)–1.92 (1) Å [43], Nb₃(μ-O)₂(μ, η²-OCMe₂CMe₂O)₂(η²-OCMe₂CMe₂O)₄H, 1.927 (2)–1.933 (2) Å, Nb₄(μ-O)₂(μ₃-O)₂(μ, η²-OCMe₂

$\text{CMe}_2\text{O})_2(\text{O}^i\text{Pr})_8$, 1.848 (6)–2.054(6) Å [44] and $[\text{Nb}_4(\mu\text{-O})_4(\mu\text{-}\eta^2\text{-O}_2\text{CMe}=\text{CH}_2)_4(\text{OPr}^i)_8]$, 1.889 (3)–1.936 (3) Å [45].

The shortest lengths in **I** are Ta–O_{ethoxy}, 1.875 (4)–1.896 (4) Å and they are comparable with Nb–O_{ethoxy} bond lengths, 1.882 (2)–1.897 (2) Å in **II**. They are identical with terminal M–O_{alkoxy} bond lengths in the $[(\mu\text{-CH}_3\text{C}(\text{CH}_2\text{O})_2\text{-C}(\text{O})\text{O})\text{Nb}_2(\mu\text{-O})(\text{OEt})_5]_2$, 1.866 (5)–1.892 (5) Å, $[(\mu\text{-CH}_3\text{C}(\text{CH}_2\text{O})_3)\text{Nb}(\text{OEt})_2]_2$, 1.860 (3) and 1.904 (3) Å [4], $[\text{Nb}(\text{C}_9\text{H}_6\text{NO})(\text{OEt})_4]_2$, 1.886 (5)–1.908 (4) Å [37], $\text{Nb}_2(\text{O})(\text{O}_2\text{CCMe}_3)_2(\text{OCH}_2\text{CMe}_3)_6$, 1.820 (11)–1.909 (11) Å, $\text{Ta}_2(\text{O}_2\text{CCH}_2\text{CMe}_3)_2(\text{OCH}_2\text{CMe}_3)_8$, 1.880 (3)–1.892 (3) Å, $\text{Ta}_2(\text{O})(\text{O}_2\text{CCMe}_3)_2(\text{OCH}_2\text{CMe}_3)_6$, 1.817 (16)–1.908 (12) Å [40], $[\text{Ta}_5(\mu_3\text{-O})_4(\mu\text{-O})_3(\mu\text{-OBU}^f)(\text{OBU}^f)_{10}]$, 1.813 (18)–1.905 (19) Å [41], $\text{Nb}_6(\mu\text{-O})_3(\mu\text{-O}_2\text{CCF}_3)_6(\mu\text{-OC}_2\text{H}_5)_6(\text{OC}_2\text{H}_5)_6$, 1.855 (4)–1.876 (4) Å [42], $\text{Nb}_4\text{O}_4(\text{OA-c})_4(\text{OPr}^i)_8$, 1.81 (1)–1.89 (1) Å [43], $[\text{Nb}_4(\mu\text{-O})_4(\mu\text{-}\eta^2\text{-O}_2\text{CMe}=\text{CH}_2)_4(\text{OPr}^i)_8]$, 1.840 (3)–1.889 (3) Å [45], $[\text{Nb}_4(\mu, \eta^1, \eta^2\text{-OC}_2\text{H}_4\text{O})_2(\mu_3, \eta^1, \eta^2\text{-OC}_2\text{H}_4\text{O})_2(\mu\text{-OC}_2\text{H}_4\text{O})(\text{OPr}^i)_{10}]$, 1.84 (1)–1.91 (1) Å [46], $[\text{Ta}_8(\mu_3\text{-O})_2(\mu\text{-O})_8(\mu\text{-OEt})_6(\text{OEt})_{14}]$, 1.848 (14)–1.891 (14) Å, $[\text{Ta}_7(\mu_3\text{-O})_3(\mu\text{-O})_6(\mu\text{-OPr}^i)_4(\text{OPr}^i)_{13}]$, 1.838 (13)–1.905(12) Å [47], $[\text{Ta}(\text{OCH}_3)_4(\text{Me}_2\text{CHCH}_2\text{CO}_2\text{CH})]$, 1.861 (7)–1.912 (7) Å and $[\text{Ta}(\text{OCH}_3)_4(\text{MeCO}_2\text{CH})]$, 1.877 (13)–1.915(13) Å [48]. Because both Nb(OEt)₅ and Ta(OEt)₅ are liquid at room temperature no crystal structure data available, therefore, structural parameters of present structure cannot be compared with the M–O_{ethoxy} bond length of them. But there are significant differences in M–O_{ethoxy} bond lengths of $[\text{Nb}(\mu\text{-OEt})(\text{OCH}_2\text{CMe}_3)_4]_2$, 1.885 (6)–1.903 (7) Å [4], $\text{Nb}_2(\text{OCH}_3)_{10}$, 1.875 (5)–1.912 (8) Å [48], $\text{Ta}_2(\text{OMe})_2(\text{O}^i\text{Pr})_8$, 1.815(8)–1.895(6) Å [49], $\text{Nb}_2(\mu\text{-OMe})_2(\text{OPr}^i)_8$, 1.797 (19)–1.963 (18) Å [50]. Interestingly, some of the M–O_{alkoxy} bond lengths in aforementioned compounds significantly are longer than that of observed in present structure and other modified metal alkoxides. Therefore, at this time we cannot conclude that the chelations shorten or elongate the M–O_{alkoxy} in Ta or Nb alkoxides in spite of the Zr and Ti alkoxides controversy [51]. On the other hand, compounds resulting from modification of Nb or Ta ethoxides with salicylaldehyde are not sensitive to moisture which suggests that the nature of M–N bonds that result from coordination of nitrogen atom to metal alkoxides is different significantly than the nature of M–O bonds result from chelating of oxygen atom.

The O(7)–Ta(1)–O(3), O(8)–Ta(1)–N(1), O(9)–Ta(1)–O(2), O(5)–Ta(2)–N(2), O(6)–Ta(2)–O(1) and O(9)–Ta(2)–O(4) angles in **I**, 169.10 (15), 165.20 (16), 156.83 (14), 170.42 (17), 165.68 (15) and 156.58 (15), respectively, are bent severely and similar to O(4)–Nb(1)–O(6), O(3)–Nb(1)–N(1), O(1)–Nb(1)–O(9), O(7)–Nb(2)–N(2), O(2)–Nb(2)–O(8) and O(5)–Nb(2)–O(9) angles in **II**, 167.4 (1), 164.7 (1), 155.8 (1), 171.0 (1), 164.8 (1) and 155.5 (1)°, respectively. The oxo-bridge angle in **I** and **II**, Ta(1)–O(9)–Ta(2), 128.00 (18)° and Nb(1)–O(9)–Nb(2), 129.4 (1)°, are somewhat wider than those reported for $[(\mu\text{-CH}_3\text{C}(\text{CH}_2\text{O})_2\text{C}(\text{O})\text{O})\text{Nb}_2(\mu\text{-O})(\text{OEt})_5]_2$, 114.4 (2)° [4] and $[\text{Ta}_5(\mu_3\text{-O})_4(\mu\text{-O})_3(\mu\text{-OBU}^f)(\text{OBU}^f)_{10}]$, 100.6 (7)–111.7 (8)° [41] and $\text{Nb}_3(\mu\text{-O})_2(\mu, \eta^2\text{-OCMe}_2\text{CMe}_2\text{O})_2(\eta^2\text{-OCMe}_2\text{CMe}_2\text{O})_4\text{H}$, 112.1 (1)°, $\text{Nb}_4(\mu\text{-O})_2(\mu_3\text{-O})_2(\mu, \eta^2\text{-OCMe}_2\text{CMe}_2\text{O})_2(\text{O}^i\text{Pr})_8$, 108.9 (3)° [44]. On the other hand they are much narrower than similar angles in $\text{Nb}_2(\text{O})(\text{O}_2\text{CCMe}_3)_2(\text{OCH}_2\text{CMe}_3)_6$, 144.0 (4)°, $\text{Ta}_2(\text{O})(\text{O}_2\text{CCMe}_3)_2(\text{OCH}_2\text{CMe}_3)_6$, 144.7 (5)°, $[\text{Nb}(\text{O})(\text{O}_2\text{CCH}_2\text{CMe}_3)(\text{OCH}_2\text{CMe}_3)_2]_4$, 146.4 (3)°, $[\text{Ta}(\text{O})(\text{O}_2\text{CCMe}_3)(\text{OCH}_2\text{CMe}_3)_2]_4$, 140.1 (3) and 144.3 (4)° [40], $[\text{Ta}_8(\mu_3\text{-O})_2(\mu\text{-O})_8(\mu\text{-OEt})_6(\text{OEt})_{14}]$, 143.4 (5)–146.5 (6)° [41], $\text{Nb}_6(\mu\text{-O})_3(\mu\text{-O}_2\text{CCF}_3)_6(\mu\text{-OC}_2\text{H}_5)_6(\text{OC}_2\text{H}_5)_6$, 143.09 (19)–143.75 (17)° [42], $\text{Nb}_4\text{O}_4(\text{O}_2\text{CCH}_3)_4(\text{OPr}^i)_8$, 148.5 (6) and 151.2 (6)° [43] and $[\text{Nb}_4(\mu\text{-O})_4(\mu\text{-}\eta^2\text{-O}_2\text{CMe}=\text{CH}_2)_4(\text{OPr}^i)_8]$, 146.2 (2) and 150.2 (2)° [45]. Surprisingly there are three similar angles in $[\text{Ta}_7(\mu_3\text{-O})_3(\mu\text{-O})_6(\mu\text{-OPr}^i)_4(\text{OPr}^i)_{13}]$ [41], that one of them is somewhat wider, 138.6 (6)°, other one is identical, 129.3 (5)° and the last one is much narrower, 107.2(5)°, than those founded in our compounds.

The packing diagram along crystallographic a axis is shown in Fig. 3 for **I**. Two alkoxy groups from each molecule are pointed to the center of the unit cell. The packing diagram of **II** is similar to **I**. In both compounds, there are four types of intermolecular interaction that appear to be hydrogen bonds. Three of them are along of crystallographic c axis, C_{aromatic}–H···O_{phenolic}, C_{iminic}–H···O_{phenolic} and C_{aromatic}–H···O_{ethoxy} and the fourth one, C_{aromatic}–H···O_{ethoxy}, is along of crystallographic a axis as shown in Figs. 4 and 5, respectively. The contact lengths and angles of these interactions in **I** are listed in Table 3. All of the interaction lengths in **I**, H3···O4: 2.56 (1) Å, H8···O2: 2.50 (1) Å, H5···O6: 2.51 (1) Å and H12···O8: 2.59 (1) Å and in **II**, H5···O5: 2.56 (4) Å, H18···O1: 2.53 (3) Å, H14···O3: 2.63 (1) Å and H3···O8: 2.57 (5) Å are somewhat longer than

Table 3
Hydrogen Bonding lengths [Å] and angles [°] for compounds **I** and **II**.

D–H...A	H...A (Å)	D...A (Å)	D–H...A (°)
In compound I			
C(aromatic)–H...O(phenolic): C3–H3...O4 ⁱ	2.56 (1)	3.28 (2)	135.0 (7)
C(iminic)–H...O(phenolic): C8–H8...O2 ⁱⁱ	2.50 (1)	3.34 (8)	151.0 (8)
C(aromatic)–H...O(ethoxy): C5–H5...O6 ⁱⁱⁱ	2.51 (1)	3.31 (8)	145.0 (9)
C(aromatic)–H...O(ethoxy): C12–H12...O8 ^{iv}	2.59 (1)	3.29 (6)	133.0 (9)
In compound II			
C(aromatic)–H...O(phenolic): C5–H5...O5 ^v	2.56 (4)	3.30 (8)	135.3 (4)
C(iminic)–H...O(phenolic): C18–H18...O1 ^{vi}	2.53 (3)	3.39 (1)	150.1 (8)
C(aromatic)–H...O(ethoxy): C14–H14...O3 ^{vii}	2.63 (1)	3.36 (7)	134.6 (3)
C(aromatic)–H...O(ethoxy): C3–H3...O8 ^{viii}	2.57 (5)	3.39 (1)	144.2 (4)

Symmetry code: i: 1 – X, 1 – Y, –Z; ii: 1 – X, –Y, 1 – Z; iii: X, Y – 1, +Z; iv: X, 1 + Y, Z; v: 1 – X, 2 – Y, 1 – Z; vi: 2 – X, 2 – Y, 1 – Z; vii: 1 – X, 1 – Y, 1 – Z.

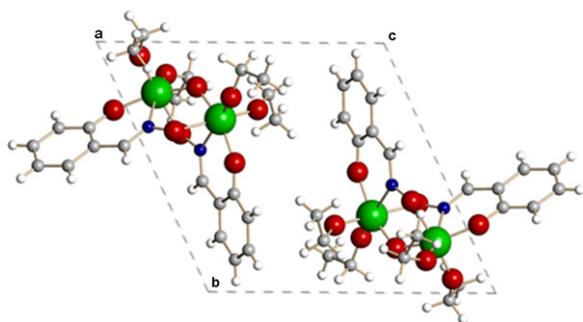


Fig. 3. Packing diagram of **I** along crystallographic a axis.

those reported for intermolecular hydrogen bonding in salicylaldoxime, 1.99 (2) Å and 2.01 (2) Å, [13]. In spite of longer interaction distances in **I** and **II** in comparison with such an interaction in salicylaldoxime it seems they have significant impact in the crystal packing. The isolated complexes are air stable and soluble in benzene, toluene,

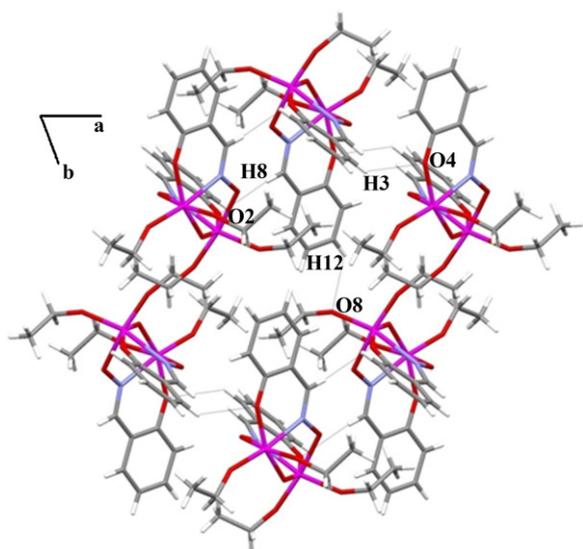


Fig. 4. Hydrogen bonding interactions of **I** along crystallographic c axis.

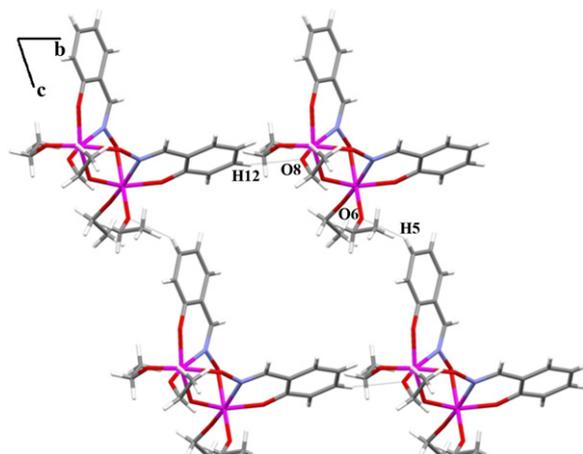


Fig. 5. Hydrogen bonding interactions of **I** along crystallographic a axis.

dichloromethane and chloroform which make them attractive precursors for the preparation of niobium and tantalum oxide by sol-gel process. However, it must be mentioned that our preliminary study shows that these compounds are more stable toward hydrolysis in comparison to parent alkoxide complexes and a harsh condition is require for hydrolytic cleavage.

4.3. Supplementary materials

CCDC 754001 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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