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**Synthesis, crystal structure and vibrational spectrum of
2,3,5-triphenyltetrazolium hexachloroniobate(V) and
oxotetrachloroniobate(V) acetonitrile, [TPT] [NbCl₆]
and [TPT] [NbOCl₄(CH₃CN)]**

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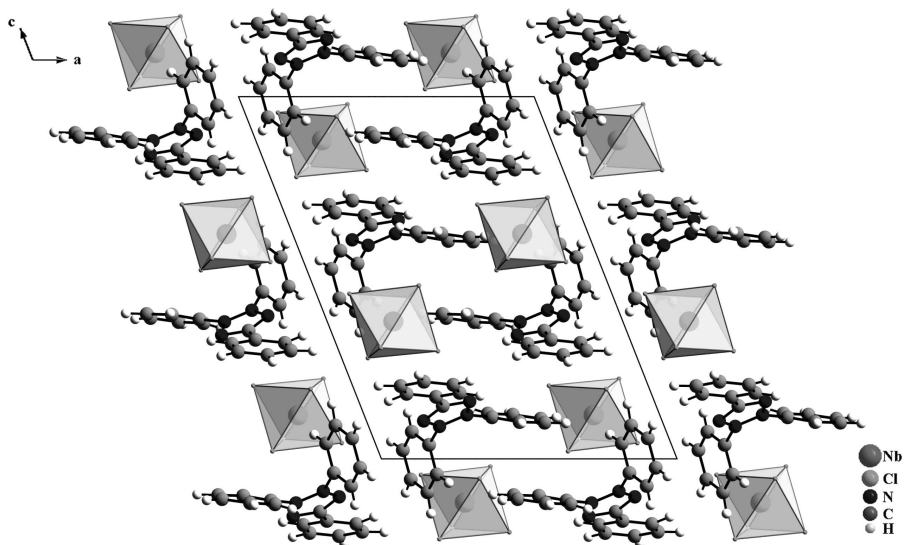


**Synthesis, crystal structure and vibrational spectrum of
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 and oxotetrachloroniobate(V) acetonitrile, [TPT] [NbCl₆]
 and [TPT] [NbOCl₄(CH₃CN)]**

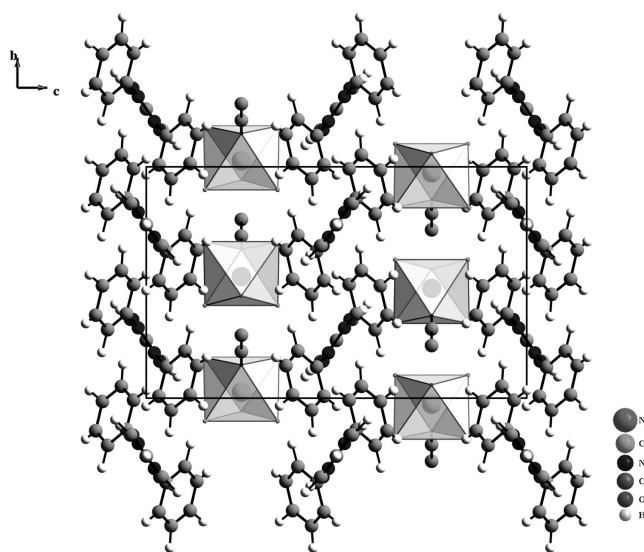
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Keywords:	2,3,5-Triphenyltetrazolium hexachloroniobate(V), 2,3,5-Triphenyltetrazolium oxotetrachloroniobate(V) acetonitrile, Crystal structure, Raman, IR/FIR



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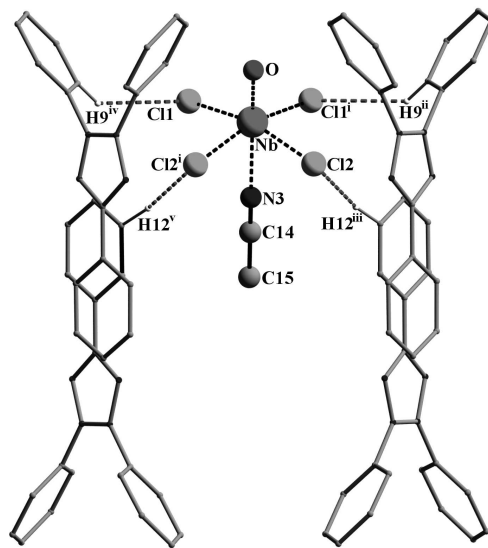


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Table 1 Crystal data and structure refinement of [TPT] [NbCl₆] (1) and [TPT] [NbOCl₄] (2)

Empirical formula	C ₁₉ H ₁₅ Cl ₆ N ₄ Nb	C ₂₁ H ₁₈ Cl ₄ N ₅ NbO
Crystal color	yellow	yellow
Formula weight/g mol ⁻¹	604.96	591.09
Crystal size/mm ³	0.28 x 0.26 x 0.25	0.30 x 0.29 x 0.26
Crystal system	monoclinic	orthorhombisch
Space group	<i>P2₁/c</i>	<i>Pbcm</i>
<i>a</i> /pm	1321.6(3)	1574.4(1)
<i>b</i> /pm	1080.7(2)	1047.7(1)
<i>c</i> /pm	1740.2(4)	1723.4(1)
β /°	111.54(2)	90.00
<i>V</i> /pm ³ · 10 ⁶	2311.8(8)	2842.6(4)
<i>Z</i>	4	4
<i>D</i> _{calculated} /g cm ⁻³	1.738	1.374
μ _{Mo-Kα} /mm ⁻¹	1.229	0.819
<i>F</i> (000)	1200	1172
Temperature /K	223(2)	223(2)
Diffractometer	Stoe IPDS 2	Stoe IPDS 2
Monochromator	Graphite	Graphite
Wavelength /pm	71.073	71.073
2θ range /°	1.00 – 25.02	1.00 – 25.03
Index ranges	-15 ≤ <i>h</i> ≤ 15	-18 ≤ <i>h</i> ≤ 18
	-12 ≤ <i>k</i> ≤ 12	-11 ≤ <i>k</i> ≤ 12
	-20 ≤ <i>l</i> ≤ 20	-19 ≤ <i>l</i> ≤ 20
Unique reflections	4087	2612
Data / refined parameters	4087 / 331	2612 / 180
Goodness-of-fit on <i>F</i> ²	0.984	1.159
<i>R</i> ₁ (<i>I</i> ≥ 2σ(<i>I</i>))	0.0543	0.0631
<i>wR</i> ₂ (<i>I</i> ≥ 2σ(<i>I</i>))	0.0973	0.1070
<i>R</i> ₁ (all data)	0.0812	0.0731
<i>wR</i> ₂ (all data)	0.1194	0.1226
Largest diff. peak and hole Peak / e · pm ⁻³	0.880 / -1.139	0.698 / -1.252

Table 2 Selected internuclear distances / pm and angles / ° for [TPT] [NbCl₆] (**1**) and [TPT] [NbOCl₄] (**2**)

Compound 1			
Nb – Cl(1)	232.1(2)	Nb – Cl(4)	235.2(2)
Nb – Cl(2)	232.1(2)	Nb – Cl(5)	236.4(2)
Nb – Cl(3)	234.6(2)	Nb – Cl(6)	239.4(2)
Cl(1) – Nb – Cl(2)	92.4(1)	Cl(2) – Nb – Cl(3)	90.7(1)
Cl(1) – Nb – Cl(3)	89.7(1)	Cl(2) – Nb – Cl(4)	89.8(1)
Cl(1) – Nb – Cl(4)	90.7(1)	Cl(2) – Nb – Cl(5)	90.8(1)
Cl(1) – Nb – Cl(5)	176.9(1)	Cl(2) – Nb – Cl(6)	177.9(1)
Cl(1) – Nb – Cl(6)	89.7(1)	Cl(3) – Nb – Cl(4)	179.4(1)
Compound 2			
Nb – O	169.6(6)	Nb – Cl(2)	239.8(2)
Nb – Cl(1)	239.1(2)	Nb – Cl(2) ⁱ	239.8(2)
Nb – Cl(1) ⁱ	239.1(2)	Nb – N(3)	245.8(8)
Cl(1) – Nb – O	98.1(2)	Cl(1) – Nb – Cl(2) ⁱ	89.1(1)
Cl(2) – Nb – O	97.6(2)	Cl(1) – Nb – N(3)	82.3(2)
N(3) – Nb – O	179.4(3)	Cl(2) – Nb – Cl(2) ⁱ	86.7(1)
Cl(1) – Nb – Cl(1) ⁱ	90.8(1)	Cl(2) – Nb – N(3)	82.0(1)
Cl(1) – Nb – Cl(2)	164.2(1)	N(3) – Nb – Cl(1) ⁱ	82.3 (2)

i) x, y, -z + 1.5; ii) -x+1, y+1/2, z+1, iii) x, -y+1/2, -z+1; iv) -x+1, y+1/2, -z+1/2; v) x, -y+1/2, z+1/2.

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7 **Synthesis, crystal structure and vibrational spectrum of 2,3,5-triphenyltetrazolium**
8 **hexachloroniobate(V) and oxotetrachloroniobate(V) acetonitrile, [TPT] [NbCl₆]**
9 **and [TPT] [NbOCl₄(CH₃CN)]**
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14 Mimoza Gjikaj*, Tao Xie and Wolfgang Brockner

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17 Clausthal-Zellerfeld, Institut für Anorganische und Analytische Chemie der Technischen Universität
18 Clausthal
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21 Received, 2009
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24 **Abstract.** Single crystals of 2,3,5-triphenyltetrazolium hexachloroniobate(V), [TPT]
25 [NbCl₆], (**1**) and of 2,3,5-triphenyltetrazolium oxotetrachloroniobate(V), [TPT]
26 [NbOCl₄(CH₃CN)], (**2**) could be obtained and their crystal structures determined. The
27 yellow compound **1** crystallizes in the monoclinic space group $P2_1/c$ (C_{2h}^5 , no. 14) with
28 $a = 1321.6(3)$, $b = 1080.7(2)$, $c = 1740.2(4)$ pm, $\beta = 111.54(2)^\circ$, and $Z = 4$. Its structure
29 is isotypic to that of the recently characterized [TPT] [SbCl₆] and built up by [TPT]⁺
30 cations and octahedral [NbCl₆]⁻ anions. The light yellow compound **2** crystallizes in the
31 orthorhombic space group $Pbcm$ (D_{2h}^{11} , no. 57) with $a = 1574.4(1)$, $b = 1047.7(1)$, $c =$
32 $1723.4(1)$ pm, and $Z = 4$. The ionic compound contains [TPT]⁺ cations and
33 [NbOCl₄(CH₃CN)]⁻ anions. The nitrogen atom of the acetonitrile solvate molecule is
34 coordinated to the niobium ion in the *trans*-position to the oxo ligand. The Nb–O bond
35 length of 169.6 pm corresponds to a double bond. The [TPT] [NbOCl₄(CH₃CN)]
36 formation proceeds with the hydrate [TPT]Cl · H₂O obvious *via* NbOCl₃. The FT-
37 Raman and FT-IR/FIR spectra of both compounds have been recorded and interpreted,
38 especially with respect to the inorganic structure parts. The melting temperatures of **1**
39 and **2** are given.
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54 **Keywords:** 2,3,5-Triphenyltetrazolium hexachloroniobate(V); 2,3,5-Triphenyltetra-
55 zolium oxotetrachloroniobate(V) acetonitrile; Crystal structure; Raman; IR/FIR
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Introduction

Crystalline niobium pentachloride, consisting of dimeric $\text{Nb}_2\text{Cl}_{10}$ units, forms with the heavier alkali chlorides MCl ($\text{M} = \text{K}, \text{Rb}$ and Cs) $\text{M}[\text{NbCl}_6]$ compounds with octahedral $[\text{NbCl}_6]^-$ units [1-3]. In case of $\text{Na}[\text{NbCl}_6]$ and of the low temperature $\text{K}[\text{NbCl}_6]$ phase [2], another still unknown crystal structure is formed according to X-ray Guinier and Raman spectroscopic investigations [2, 3]. This is in accordance to the respective phase diagrams of the $\text{NbCl}_5 - \text{MCl}$ systems [3, 4]. Secondly, the existence of from $[\text{NbCl}_6]^-$ deviating species as e.g. $[\text{Nb}_2\text{Cl}_{11}]^-$ in dependency of the $\text{NbCl}_5 : \text{Cl}$ stoichiometry is still open [5]. The formation of such “acidic” $[\text{Nb}_2\text{Cl}_{11}]^-$ species out of $\text{Nb}_2\text{Cl}_{10} + \text{Cl}^-$ would be analogous to the formation of well known $[\text{Al}_2\text{Cl}_7]^-$ ions [6, 7]. The large $[\text{TPT}]^+$ ion could influence the kind of the chloroniobate(V) species in the reaction of NbCl_5 with $[\text{TPT}]^+ [\text{Cl}]^-$.

Moreover, $[\text{TPT}]\text{Cl}$ is hygroscopic and reacts with moisture to a triphenyltetrazolium chloride hydrate, $([\text{TPT}]\text{Cl} \cdot \text{H}_2\text{O})$ [8]. Besides its chloride ion donor properties this hydrate can form oxohalide compounds with water sensitive halides. In such a reaction fortunately and more fortuitously single crystals of $[\text{TPT}] [\text{NbOCl}_4 (\text{CH}_3\text{CN})]$ could be obtained. Obviously, the formation reaction proceeds *via* NbOCl_3 . The crystalline triphenylmethylphosphonium oxotetrachloroniobate(V), $[\text{Ph}_3\text{MeP}]^+ [\text{NbOCl}_4 (\text{CH}_3\text{CN})]^-$, characterized until now only, was synthesized by an intricate route *via* NbCl_5 with CCl_3NO_2 [9]. Another way to oxotetra-chloroniobates(V) runs *via* a synproportionation of niob(V)oxides with NbCl_5 in the presence of CsCl in molten salt state [10]. The all together rare oxotetrachloroniobate(V) unit is found furthermore in the uncommon compounds $[(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CNCMe}_3)_4\text{Cl}] [\text{NbOCl}_4(\text{THF})] \cdot (\text{THF})$ [11] and in $\text{Te}_6(\text{NbOCl}_4)_2$ [12]. With the obtaining of single crystals of the title compounds the opportunity is used to investigate and characterize the new compounds in more detail.

Results and Discussion

Crystal Structure of [TPT][NbCl₆] (1)

Treatment of niobium pentachloride, NbCl₅, with one equivalent of anhydrous 2,3,5-triphenyltetrazolium chloride in acetonitrile afforded [TPT] [NbCl₆] (**1**) as yellow crystals. The product shows rapid decomposition on the slightest exposure to the atmosphere, but the crystals were manipulated under argon.

The complex salt **1** crystallizes in the monoclinic space group *P*2₁/*c* (no. 14) with four formula units per unit cell. The asymmetric unit contains isolated [TPT]⁺ cations and [NbCl₆]⁻ anions and its structure is isotypic with [TPT] [SbCl₆] [13] (Fig. 1 and Tab. 1).

Figure 1

Table 1

The packing diagram of **1** shows the face-to-face stacked orientation between the phenyl rings of the two neighboring molecules, which is caused by intermolecular $\pi\cdots\pi$ interactions. The closest contact between the neighboring phenyl rings is 369 pm, and it is similar to that found in [TPT] [SbCl₆] [13].

In the cationic unit the five atoms in the tetrazolium ring (N(1), N(2), N(3), C(4) and N(5)) are coplanar. N(1) – N(5) and N(2) – N(3) are equivalent (131 pm). The N(1) – N(2) bond is much longer than the former two bonds (2.0 pm). The elongation of this bond may be ascribed to the repulsion between the relevant phenyl groups. The deviations of C(6), C(12) and C(18) atoms from the tetrazolium plane are 5.4, –35.4 and 19.9 pm, respectively. The torsion angles of C(6), C(12) and C(18) phenyl rings are 94.31, –36.81 and 22.05°, respectively. These values agree well with those reported for [TPT] [SbCl₆] [13].

The hexachloroniobate anion is approximately octahedral coordinated by six chlorine atoms. The metal–chlorine bond distances range from 232.1(2) to 239.4(2) pm (mean

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6 value of 235.0 pm). The *cis*-Cl – Nb – Cl angles range from 89.7 to 92.4°, and *trans*-Cl
7 – Nb – Cl angles of 176.9 and 179.4° in the equatorial positions, and 177.9° in the axial
8 positions (Tab. 2). These values agree with those of reported hexachloroniobate(V) salts
9 [14-17].
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14 **Table 2**
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22 ***Crystal Structure of [TPT] [NbOCl₄(CH₃CN)] (2)***
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25 Reaction of 2,3,5-triphenyltetrazolium chloride monohydrate with NbCl₅ in 1:1 ratio led
26 to precipitation of yellow crystals of title compound **2**. [TPT] [NbOCl₄(CH₃CN)]
27 crystallizes in the orthorhombic space group *Pbcm* (no. 57) with four formula units per
28 unit cell. The crystal structure of **2** consists of discrete [TPT] cations and
29 [NbOCl₄(CH₃CN)] anions (Fig. 2).
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34 **Figure 2**
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37 The [NbOCl₄(CH₃CN)]⁻ ion has C_{4v} symmetry long known for oxotetrahalometallate
38 anions of the early transition metals [18, 19]. The niobium atom is displaced by 33 pm
39 toward the oxo ligand from the best mean plane through the four chlorine atoms. The
40 short Nb–O bond of 169.6 pm is comparable to those found for [(η⁵-
41 C₅H₅)Nb(CNCMe₃)₄Cl][NbOCl₄(THF)] · THF [11] and Tl[NbOCl₄] [20] and indicates
42 multiple bond character while in the *trans*-position the long Nb–N(3) bond of 245.8 pm
43 indicates only weak bonding (Fig. 3 and Tab. 2). The coordination of the acetonitrile
44 molecule is linear with Nb–N(3)–C(14) of 178.9 and N(3)–C(14)–C(15) of 179.1°. The
45 Nb–Cl bond lengths range from 239.1 to 239.8 pm. The *cis*-Cl – Nb – Cl angles range
46 from 86.7(1) to 90.8°, and the *trans*-Cl – Nb – Cl angle is 164.2° in the equatorial
47 positions and they compare well with those of known hexachloro-niobate(V) salts [9,
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6 The contacts between anions and cations [C(12)–H(12)···Cl(2) 376.0(1) pm, C(9)–
7 H(9)···Cl(1) 376.7(1) pm] exist as weak C – H ··· Cl interactions involving four [TPT]⁺
8 cations and one one [NbOCl₄(CH₃CN)][−] anion [22]. The whole structure can also be
9 seen as being from alternating layers along *b* axes, in which the [TPT]⁺ cations and the
10 [NbOCl₄(CH₃CN)][−] anions are linked by hydrogen bonds (Fig. 3).
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16 **Figure 3**

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23 **Vibrational spectra and assignment**

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27 *2,3,5-Triphenyltetrazolium hexachloroniobate(V), [TPT][NbCl₆], (1)*

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31 According to the crystal structure determination the title compound **1** is built up by
32 [TPT]⁺ cations and [NbCl₆][−] anions. These units can be clearly detected in the
33 vibrational spectra of **1** (Fig. S1 / Supporting information).
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35 The relevant vibrational modes of [NbCl₆][−] are summarized in Table 3 along with the
36 proposed assignment and in comparison to literature data [2, 23].
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41 **Table 3**

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45 The [TPT] cation exhibits approximately C₂ symmetry, therefore all its vibrations are
46 Raman active and infrared allowed, what is also verified by its whole vibrational
47 spectrum. The [TPT]⁺ vibrations result in their characteristic modes for the aromatic -
48 C–H stretchings and bendings as well as for the phenyl ring and the tetrazolium
49 heterocyclus modes. The corresponding Raman as well as IR bands are very similar to
50 those of [TPT]⁺ [Cl][−] [24] and [TPT] [SbCl₆] [13]. The relevant [TPT]⁺ Raman and IR
51 modes may be taken from footnote 1.
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Octahedral $[\text{NbCl}_6]^-$ units (O_h symmetry) are here the more interesting inorganic components of the crystal structure of **1**. A vibrational analysis for such a unit results in [25]:

$$\Gamma_{\text{vib}}([\text{NbCl}_6]^- / O_h) = A_{1g}(\text{RE}) + E_g(\text{RE}) + 2 F_{1u}(\text{IR}) + F_{2g}(\text{RE}) + F_{2u}(\text{i.a.}),$$

with RE = Raman, IR = Infrared and i.a. = inactive, and with $A_{1g} + E_g + F_{1u}$ as stretchings and $F_{1u} + F_{2g}$ as bendings.

The Raman as well as the IR/FIR spectra of **1** do not exhibit the expected pattern of a $[\text{MCl}_6]$ octahedron, but they show much more vibrational modes. It is also noteworthy that the selection rules and the rule of mutual exclusion do not have an effect, so that the $[\text{NbCl}_6]^-$ fundamentals appear in the Raman as well as FIR spectrum. According to the crystal structure determination, the $[\text{NbCl}_6]^-$ ion is built up octahedrally, so that the sketched peculiarities are caused by symmetry lowering of the anion by the crystal lattice of **1** (removal of degeneracy). (In the monoclinic [TPT] $[\text{NbCl}_6]^-$: $P2_1/c$ (C_{2h}^5), Nb is on the general position of $4e$, what means site symmetry C_1 for Nb *respective* $[\text{NbCl}_6]^-$).

In detail, the very strong Raman mode at 370 cm^{-1} and the medium FIR band at 372 cm^{-1} can be assigned to ν_1 in A_{1g} (Table 3). The very strong and remarkable broad FIR bands at $341/331 \text{ cm}^{-1}$ show a Raman counterpart at 339 cm^{-1} and they belong to ν_3 / F_{1u} . ν_2 / E_g is split and existent not only in Raman but also in FIR spectrum. The bending mode ν_5 / F_{2g} , in Raman at 173 cm^{-1} , is present in FIR spectrum and it is split. Only ν_4 / F_{1u} appears in the FIR spectrum at 161 cm^{-1} as a very strong band. Altogether, our presented vibrational data are in agreement with these given in [2, 23], as well as with those of $[\text{Et}_4\text{N}]^+ [\text{NbCl}_6]^-$ [26]. Further details may be obtained from Tab. 3.

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6 ***2,3,5-Triphenyltetrazolium oxotetrachloroniobate(V) acetonitrile adduct,[TPT]***
7 ***[NbOCl₄(CH₃CN)], (2)***
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11 Title compound **2** is built up by [TPT] cations, [NbOCl₄ (CH₃CN)] anions. Additional
12 acetonitrile solvate molecules are included in the crystals, likely as fluid inclusions. In
13 the vibrational spectra of **2** the mentioned building components can be clearly
14 recognized. The acetonitrile is weakly coordinated to Nb in the complex anion
15 confirmed by the Nb–N distance 245.8 pm. The two different acetonitrile components
16 can be clearly distinguished by their CN- stretchings in the range 2320-2250 cm⁻¹.
17 Raman and IR bands in this region are split due to Fermi resonance [27] and shifted by
18 about 20 cm⁻¹ to higher wave numbers in comparison to these ones of liquid acetonitrile
19 [28-30] and in accordance to other weak bounded acetonitrile adducts [19, 31].
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29 The Raman and IR/FIR spectra of crystalline compound **2** are shown in Fig. S2 /
30 Supporting information. In this contribution, the main interest is directed on the
31 inorganic [NbOCl₄]⁻ respective [NbOCl₄(CH₃CN)]⁻ group. Therefore, the relevant
32 [NbOCl₄]⁻ vibrational modes of crystalline **2** in the spectral region below 1000 cm⁻¹ are
33 presented in Table 4 along with their estimated intensities and the proposed assignment.
34 All the vibrational frequencies of compound **2** with marked peculiarities (in parenthesis)
35 are given as footnote 2 below Table 4 as well as the values of acetonitrile for
36 completeness reasons.
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45 **Table 4**
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49 As in title compound **1**, the [TPT]⁺ vibrations of **2** are Raman active and infrared
50 allowed and they are found in the characteristic group frequency ranges. The [TPT]⁺
51 Raman as well as IR bands are very similar to those in [TPT] [NbCl₆] (c.f. footnote 1),
52 [TPT]⁺ [Cl]⁻ [24] and in [TPT][SbCl₆] [13]. All the relevant [TPT]⁺ Raman and IR
53 modes are summarized in footnote 2.
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Due to the weak acetonitrile coordination the anionic spectral parts are best interpreted by $[\text{NbOCl}_4]^-$ units rather than by $[\text{NbOCl}_4(\text{CH}_3\text{CN})]^-$ ions as in the first structurally characterized saltlike complex triphenylmethylphosphonium oxotetrachloroniobate(V) acetonitrile, $[\text{Ph}_3\text{MeP}]^+ [\text{NbOCl}_4(\text{CH}_3\text{CN})]^-$ [9]. The square pyramidal $[\text{NbOCl}_4]^-$ group exhibits C_{4v} symmetry. A vibrational analysis for this unit results in [32]:

$$\Gamma_{\text{vib}}([\text{ONbCl}_4]^- / C_{4v}) = 3 A_1 (\text{IR, RE}) + 2 B_1 (\text{RE}) + B_2 (\text{RE}) + 3 E (\text{IR, RE}),$$

with IR = Infrared and RE = Raman, and with $2 A_1 + B_1 + E$ as stretchings and the remaining $A_1 + B_1 + B_2 + 2 E$ as bendings.

The Raman and IR/FIR frequencies for $[\text{NbOCl}_4(\text{CH}_3\text{CN})]^-$ in crystalline $[\text{Ph}_3\text{MeP}][\text{NbOCl}_4(\text{CH}_3\text{CN})]$ are given and assigned in part only [9]. Furthermore, $\text{NbOCl}_3\text{-NbCl}_5\text{-CsCl}$ melts have been investigated by Raman spectroscopy [10] and the characteristic $[\text{NbOCl}_4]^-$ frequencies were determined therefrom. The given interpretation of the Raman data has been assisted by quantum mechanical *ab initio* SCF (Self Consistent Field) calculations. The included calculations of the $[\text{NbOCl}_4]^-$ frequencies and their PED (Potential Energy distribution) values were done with help of the programs GAMFORCE [33] and MOLVIB [34].

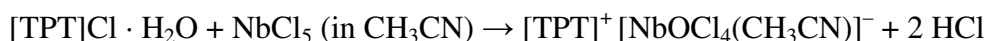
In the Table 4 our $[\text{NbOCl}_4]^-$ vibrational modes of crystalline **2** are presented along their proposed assignment based on the mentioned PED data and in comparison to the vibrational frequencies of $[\text{NbOCl}_4]^-$ given in [10]. According to that (Fig. S2 and Table 4) $\nu(\text{Nb}=\text{O})$ is proved by the strong band at 945 and 955 cm^{-1} , respectively. The bands at 341/330 and 244/243 cm^{-1} belong to NbCl_4 stretchings whereas these ones at 168/175 cm^{-1} are NbCl_4 bendings. The Raman band at 140 cm^{-1} is attributed to a ONbCl_4 bending. Bands below 100 cm^{-1} may be ascribed to so-called lattice vibrations. Herewith our proposed assignment of the anionic unit differs considerable from this one of the $[\text{Ph}_3\text{MeP}]^+$ salt [9] especially due to the differences in the FIR spectra.

Concluding remarks

Two new niobate compounds, 2,3,5-triphenyltetrazolium hexachloroniobate(V) (**1**) and oxo-tetrachloroniobate(V) acetonitrile (**2**), have been synthesized. The identity and purity of the synthesized compounds were confirmed by elemental analysis, infrared and Raman spectroscopy, and single X-ray diffraction.

In compound **1**, no hydrogen bonds are found between the octahedral $[\text{NbCl}_6]^-$ anions and 2,3,5-triphenyltetrazolium cations.

Title compound **2** could be obtained by the reaction of $[\text{TPT}]\text{Cl} \cdot \text{H}_2\text{O}$ with niobopentachloride in acetonitrile according to



As expected, $[\text{NbOCl}_4(\text{CH}_3\text{CN})]^-$ exhibits C_{4v} symmetry and Nb^{5+} is coordinated by one oxygen, four chloride ions and one acetonitrile molecule. The niobium is displaced by 33 pm toward the oxo ligand from the best mean plane through the four chlorine atoms. The short Nb–O bond of 169.6 pm indicates multiple bond character while in the *trans*-position the long Nb–N bond of 245.8 pm indicates only weak bonding. The $[\text{NbOCl}_4(\text{CH}_3\text{CN})]^-$ anion is hydrogen bonded to four 2,3,5-triphenyltetrazolium cations.

Experimental Section

Materials and Methods: All manipulations and chemical reactions were carried out in a dry argon atmosphere using standard Schlenk, vacuum-line and glove-box techniques. NbCl_5 was sublimated for purification, and 2,3,5-triphenyltetrazolium chloride monohydrate (Fluka) was used without additional purification. CH_3CN was distilled and dried by P_4O_{10} . Obviously, the commercial anhydrous $[\text{TPT}]\text{Cl}$ contained water, therefore the “anhydrous” 2,3,5-triphenyltetrazolium chloride was dried under reduced

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6 pressure in Schlenk tubes (120-130 °C, 2 h). The melting points of **1** and **2** were
7 measured on a BÜCHI 520 apparatus and they are uncorrected values.
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11 **2,3,5-Triphenyltetrazolium hexachloroniobate(V) (1):** 352.8 mg (1 mmol) [TPT]Cl ·
12 H₂O and 270.4 mg (1 mmol) NbCl₅ were mixed in a Schlenk tube. The mixture was
13 kept for at 140 °C for 3 h. Upon cooling 15 mL CH₃CN was added forming a yellow
14 clear solution. After some days the yellow, block-shaped crystals were formed.
15 C₁₉H₁₅Cl₆N₄Nb: calc. C 37.72, H 2.50, N 9.26; found C 37.32, H 2.53, N 9.10. The melting
16 temperature was found to be 128 °C.
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23 **2,3,5-Triphenyltetrazolium oxotetrachloroniobate(V) acetonitrile (2):** Compound **2**
24 was synthesized by using the same method as that for compound **1**, except for the
25 replacement of [TPT]Cl · H₂O by dried [TPT]Cl. Upon cooling to room temperature,
26 yellow, block-shaped crystals formed. C₂₁H₁₈Cl₄N₅NbO: calc. C 42.67, H 3.07, N 11.85;
27 found C 41.99, H 3.11, N 11.21. The melting temperature was found to be 154 °C.
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33 34 *X-Ray diffraction analysis*

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36 Since both compounds are sensitive towards hydrolysis by moist air and the selection of
37 crystals was performed in an argon filled glove box. Crystals were transferred into glass
38 capillaries which were sealed. The crystals selected had the size 0.28 · 0.25 · 0.20 mm³
39 for [TPT] [NbCl₆] and 0.30 · 0.26 · 0.25 mm³ for [TPT] [NbOCl₄(CH₃CN)]. All data
40 were collected on a Stoe IPDS-II single-crystal X-ray diffractometer with graphite
41 monochromated Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 223 K. Crystal structure solution
42 by direct methods using SHELXS-97 [35] yielded in all cases heavy atom positions.
43 Subsequent difference Fourier analyses and least squares refinements with SHELXL-97
44 [35] allowed localization of the remaining atom positions. The H positions of [TPT]⁺
45 were determined by a final difference Fourier Synthesis. In compound **2** the H atoms of
46 acetonitrile molecule couldn't be located. Crystal data and structure refinement
47 parameters of structures are summarized in Table 1. For the preparation of the structure
48 drawings, programs Diamond [36] and POV-Ray [37] were applied.
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Further details on the crystal structure investigations may be obtained from Cambridge Crystallographic Data CCDC 723597 for compound **1** and CCDC 723596 for compound **2**.

FT-Raman and FT-FIR/IR spectra

FT-Raman spectra were recorded from crystalline samples of the title compounds in sealed silica tubes with a Raman module FRA 106 (Nd:YAG laser, 1064 nm, 200 mW) attached to a Bruker IFS 66v interferometer. The FT-IR/FIR spectra were obtained with the mentioned interferometer from solid sample material of **1** and **2** “sandwiched” between CsI and PE pellets, respectively

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References

- [1] A. Zalkin, D. E. Sands, *Acta Crystallogr.* **1958**, *11*, 615.
- [2] H. -C. Gaebell, G. Meyer, R. Hoppe, *Z. Anorg. Allg. Chem.* **1982**, *493*, 65.
- [3] D. R. Sadoway, S. N. Flengas, *Can. J. Chem.* **1978**, *56*, 2538.
- [4] a) K. Huber, E. Jost, E. Neuenschwander, M. Studer, B. Roth, *Helv. Chim. Acta* **1958**, *41*, 2414; b) E. M. Levin, C. R. Robbins, H. F. McMurdie, Editor: M. K. Reser, *Phase Diagrams for Ceramists*, Columbus, Ohio, **1964**, p. 389.
- [5] N. Koura, H. Matsuzawa, T. Kato, y. Idemoto, F. Matsumoto, *J. Korean Electrochem. Soc.* **2002**, *5*, 183.
- [6] S. J. Cyvin, P. Klæboe, E. Rytter, H. A. Øye, *J. Chem. Phys.* **1970**, *52*, 2776.
- [7] G. Torsi, G. Mamantov, G. M. Begum, *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 553.
- [8] D. G. Golovanov, D. S. Perekalin, A. A. Yakovenko, M. Y. Antipin, K. A. Lyssenko, *Mendeleev Commun.* **2005**, *15*, 237.
- [9] W. Hiller, J. Strähle, H. Prinz, K. Dehnicke, *Z. Naturforsch.* **1984**, *39b*, 107.

- 1
2
3
4
5
6 [10] C. Rosenkilde, G. Voyiatzis, V. R. Jensen, M. Ystenes, T. Østvold, *Inorg. Chem.*
7 **1995**, *34*, 4360.
8
9 [11] H. C. Aspinall, M. M. Roberts, S. J. Lippard, *Inorg. Chem.* **1984**, *23*, 1782.
10
11 [12] J. Beck, G. Bock, *Z. Anorg. Allg. Chem.* **1996**, *622*, 823.
12
13 [13] M. Gjikaj, T. Xie, W. Brockner, *Z. Anorg. Allg. Chem.* **2009**, in press.
14
15 [14] H. N. Schäfer, H. Burzlaff, *Acta Crystallogr.* **1992**, *C48*, 795.
16
17 [15] B. Therrien, A. L. Beauchamp, *Acta Crystallogr.* **1993**, *C49*, 1301.
18
19 [16] P. J. McKarns, M. J. Heeg, C. H. Winter, *Inorg. Chem.* **1998**, *37*, 1743.
20
21 [17] R. Dübgen, U. Müller, F. Weller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1980**, *471*,
22 89.
23
24 [18] F. A. Cotton, S. J. Lippard, *J. Inorg. Chem.* **1965**, *4*, 1621.
25
26 [19] F. A. Cotton, S. J. Lippard, *J. Inorg. Chem.* **1966**, *5*, 416.
27
28 [20] J. Beck, J. Bordinhão, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1261.
29
30 [21] J. C. Dewan, D. L. Kepert, C. L. Raston, A. H. White, *J. Chem. Soc. Dalton*
31 **1975**, 2031.
32
33 [22] M. Hasan, I. V. Kozhevnikov, M. R. H. Siddiqui, A. Steiner, N. Winterton,
34 *Inorg. Chem.* **1999**, *38*, 5637.
35
36 [23] S. M. Horner, R. J. H. Clark, B. Crociani, D. B. Copley, W. w. Horner, F. N.
37 Collier, S. Y. Tyree, Jr., *Inorg. Chem.* **1968**, *7*, 1859.
38
39 [24] Sigma-Aldrich:
40
41 <http://www.sigmaaldrich.com/catalog/search/ProductDetail/Fluka/93140>
42
43 [25] J. Weidlein, U. Müller, K. Dehnicke, *Schwingungsspektroskopi*, Thieme,
44 Stuttgart – New York, **1982**, p. 139.
45
46 [26] I. R. Beattie, T. R. Gilson, G. A. Ozin, *J. Chem. Soc.* **1968**, *A*, 2765.
47
48 [27] F. W. Parker, A. H. Nielsen, W. H. Fletcher, *J. Mol. Spectrosc.* **1957**, *1*, 107.
49
50 [28] F. Menzel, W. Brockner, M. Ystenes, *J. Mol. Struct.* **1993**, *294*, 53.
51
52 [29] M. Gjikaj, W. Brockner, A. Adam, *Z. Anorg. Allg. Chem.* **2006**, *632*, 279.
53
54 [30] B. Smith, *Infrared Spectral Interpretation*, CRC Press LLC Boca Raton **1999**,
55 142.
56
57 [31] Y. Kawano, Y. Hase, O. Sala, *J. Mol. Struct.* **1976**, *30*, 45.
58
59
60

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2
3
4
5
6 [32] J. Weidlein, U. Müller, K. Dehnicke, *Schwingungsspektroskopie*, Thieme,
7 Stuttgart –New York, **1982**, p. 114.
8
9 [33] Ø. Bache, *GAMFORCE*, NTH Trondheim, Norway **1990**.
10
11 [34] T. Sundius, *J. Mol. Struct.* **1990**, 218, 321.
12
13 [35] G. M. Sheldrick, *SHELXS-97, SHELXL-97*, University of Göttingen **1997**.
14
15 [36] K. Brandenburg, *DIAMOND*, Version 3, Crystal Impact GbR, Bonn **2004**.
16
17 [37] POV-Ray, Version 3.5, Copyright by the POV-Ray-Team, Hallam Oaks Pty. Ltd
18 **1994–2004**.
19
20
21
22
23
24
25
26
27
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Table headings

Table 1 Crystal data and structure refinement of [TPT] [NbCl₆] (**1**) and [TPT] [NbOCl₄] (**2**)

Table 2 Selected internuclear distances / pm and angles / ° for [TPT] [NbCl₆] (**1**) and [TPT] [NbOCl₄] (**2**)

Table 3 Raman and FIR frequencies (cm⁻¹) of crystalline [TPT] [NbCl₆] in the [NbCl₆]⁻ relevant spectral region below 500 cm⁻¹ along with their estimated intensities and proposed assignment

Table 4 Vibrational frequencies (cm⁻¹) of [NbOCl₄]⁻ in title compound **2** in the relevant spectral region below 1000 cm⁻¹ along with their estimated intensities and proposed assignment and in comparison to literature data

Figure headings

Figure 1 View of the crystal structure of [TPT] [NbCl₆] along the *b*-axis.

Figure 2 View of the crystal structure of [TPT] [NbOCl₄(CH₃CN)] along the *a*-axis.

Figure 3 Interaction (dotted lines) between two [TPT] cations and one [NbOCl₄(CH₃CN)] anion in compound **2**. (The rest of hydrogen atoms are not displayed for clarity).

Table 3 Raman and FIR frequencies (cm^{-1}) of crystalline [TPT] $[\text{NbCl}_6]$ in the $[\text{NbCl}_6]^-$ relevant spectral region below 500 cm^{-1} along with their estimated intensities and proposed assignment

Raman	FIR	$[\text{NbCl}_6]^-$ [2, 23] ^a	Assignment / O_h mode description
370 vvs	372 m	375 vs, br	$\nu_1 / A_{1g} : \nu_s$
339 w	341 vs, br 331 vs, br	333 vs, br	$\nu_3 / F_{1u} : \nu_{as}$
292 vw			[TPT] ⁺
260 w	275 m	287 w	$\nu_2 / E_g : \nu$
246 w	268 sh		
173 s	188 vw 174 sh	182 m, sh 177 s	$\nu_5 / F_{2g} : \delta$
	161 vvs	176 s	$\nu_4 / F_{1u} : \delta$
		163 s	
137 sh	144 vvw		$(\nu_6 / F_{2u} : \delta)?$
118 sh			Lattice vibration
104 s			Lattice vibration

Estimated intensities: s: strong, m: medium, w: weak, v: very, sh: shoulder, br: broad. ν : stretching, δ : bending. ^a [2]: Raman for $[\text{TINbCl}_6]$; [23]: FIR for $[\text{KNbCl}_6]$.

Footnote 1. Raman (cm^{-1} / intensity) of crystalline [TPT] $[\text{NbCl}_6]$: 3161 vw, 3080 sh, 3068 s, 3045 sh, 1607 vvs, 1583 s, 1527 vs, 1485 m, 1457 s, 1410 sh, 1394 w, 1354 vvs, 1336 vw, 1306 w, 1285 vw, 1220 w-m, 1181 w, 1074 w, 1042 sh, 1005 vs, 993 vs, 830 vw, 729 vw, 684 vw, 624 vw, 608 vvw, 523 vvw, 406 vw, 370 vvs, 339 w, 292 vw, 260 w, 246 w, 173 s, 137 sh, 118 sh, 104 s.

IR/FIR (cm^{-1} / intensity) of crystalline [TPT] $[\text{NbCl}_6]$: 3175 vw, 3087 w, 3064 m, 3047 sh, 1608 s-vs, 1575 sh, 1528 vs, 1487 vs, 1470 sh, 1458 vvs, 1357 w-m, 1300 s, 1273 w, 1172 s, 1158 vs, 1145 m, 1105 m, 1075 m, 1030 m, 998 vs, 918 m, 788 s, 764 vvs, 755 vvs, 730 sh, 726 vvs, 687 vvs, 670 sh, 618 w, 607 vs, 520 m, 508 m-s, 490 s, 440 vvw, 423 vvw, 403 vvw, 372 m, 341 vs, br, 331 vs, br, 275 m, 268 sh, 188 vw, 174 sh, 161 vvs, 144 vvw.

Table 4 Vibrational frequencies (cm^{-1}) of $[\text{NbOCl}_4]^-$ in title compound **2** in the relevant spectral region below 1000 cm^{-1} along with their estimated intensities and proposed assignment and in comparison to literature data

Raman	IR / FIR	$[\text{NbOCl}_4]^-$ [10]	Assignment / C_{4v} , mode description
945 s	955 vs, 945 vs	942 - 962	$\nu_1 / A_1 : \nu \text{ Nb} = \text{O}$
341 m-s	330 vvs, br	312 - 333	$\nu_2 / A_1 : \nu_s \text{ NbCl}_4$
168 w	175 w	150	$\nu_3 / A_1 : \delta \text{ NbCl}_4$
		268	$\nu_4 / B_1 : \nu \text{ NbCl}_4$
		(141) calc.	$\nu_5 / B_1 : \delta \text{ NbCl}_4$
140 w-m		165	$\nu_6 / B_2 : \delta \text{ ONbCl}_4$
337 sh	330 vvs, br	313 – 315	$\nu_7 / E : \nu_{\text{as}} \text{ NbCl}_4$
244 s	243 s	232 – 237	$\nu_8 / E : \delta \text{ NbCl}_4$
		(47) calc	$\nu_9 / E : \delta \text{ ONbCl}_4 / \text{ or lattice vibration}$

Estimated intensities: s: strong, m: medium, w: weak, v: very, sh: shoulder, br: broad, ν : stretching, δ : bending.

Footnote 2. Raman (cm^{-1} / intensity) of crystalline [TPT] $[\text{NbOCl}_4(\text{CH}_3\text{CN})]$: 3166 vw, 3069 s, 3050 sh, 2935 m (AN), 2297 w-m ($\nu \text{ NC}$), 2290 vvw, sh (AN), 2272 w-m ($\nu \text{ NC}$), 2256 w (AN), 1606 vvs, 1584 s, 1530 vs, 1487 m, 1457 s, 1409 w, 1376 vs, 1337 w, 1303 w, 1278 vw, 1240 w, 1166 w-m, 1079 w, 1033 vvw, 1025 w, 1003 vs, 994 sh, 945 s ($\nu \text{ Nb} = \text{O}$), 926 w-m (AN), 833 w, 734 w, 679 w, 610 w, 519 w, 440 w (AN), 403 w, 376 w (AN + TPT), 341 m-s, 337 s, 295 vvw (TPT ?), 244 s, 168 w, 140 w-m, 95 vvs.

IR/FIR (cm^{-1} / intensity) of crystalline [TPT] $[\text{NbOCl}_4(\text{CH}_3\text{CN})]$: 3095 w, 3065 m, 2932 w (AN), 2311 sh ($\nu \text{ NC}$), 2298 m (AN), 2274 m ($\nu \text{ NC}$), 2256 w (AN), 1608 s, 1530 vs, 1486 vs, 1469 sh, 1458 vs, 1405 w, 1370 w-m, 1365 sh, 1337 vw, 1300 m, 1236 w, br, 1180 sh, 1160 vs, 1145 m, 1101 w, 1075 m-s, 1030 m-s, 1025 sh, 998 vs, 954 vs + 945 sh ($\nu \text{ Nb}=\text{O}$), 926 s (AN), 870 vw, br, 834 vw, 786 sh, 764 vvs, 730 sh, 724 s, 686 vvs, 620 vw, 608 vs, 519 m, 468 vw, 441 vvw, 330 vvs, br, 243 s, 175 m, br. [AN : Acetonitrile].

Acetonitrile: Raman (cm^{-1} / intensity): 2999 vw, 2942 vs, 2292 vw, 2251 s, 1374 vvw, 919 w, 379 vw [28].

Acetonitrile: IR (cm^{-1} / intensity): 3164 w, 3002 w-m, 2944 w, 2292 m, 2252 vs, 1444 s, 1375 s, 1039 m-s, 918 m, 750 w [28-30].