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# 5-(2-pyridil)-1H-tetrazole complexes with Mo(IV) and W(IV) cyanides.

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The reactions of tetrazole ligand derived from 2-cyanopyridine with  $K_3Na[Mo(CN)_4O_2]\cdot 6H_2O$  and  $K_3Na[W(CN)_4O_2]\cdot 6H_2O$  in water-ethanol solution result in isolation of two new complexes of formulae:  $(PPh_4)_2[Mo(CN)_3O(pdt)]\cdot 2H_2O$  (1) (pdt = 5-(2pyridil)-1H-tetrazole) and  $(PPh_4)_2[W(CN)_3O(pdt)]\cdot 3H_2O$  (2). The complexes were characterized by elemental analysis, single crystal X-ray structure measurements, IR and UV-Vis spectroscopy, cyclic voltammetry measurement as well as thermogravimetric measurement. The X-ray crystal structure measurements indicate the presence of two coordination isomers in a single crystal. The pyridine nitrogen ocupies both *trans* and/or *cis* position to the M=O bond, which is explained by similar *pK* of pyridine and tetrazole nitrogen. The DTG measurements indicate the stabilization of tetrazole upon coordination.

#### Introduction

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Tetrazoles are one of the most intensively studied nitrogen rich compounds in the last decade. This is not only connected with their application as modern primary explosives, but also they found numerous applications in medicine (for example as the acid substituent exchanging carboxylic group and thus spreading the application of known pharmaceuticals), biochemistry, material science, optronic devices, sensors etc.<sup>1</sup> Due to a variety of coordination modes, they started to be utilized in the synthesis of materials of desired properties. The coordination to a metal centre was studied at the very beginning by one of the most important synthesis method which is a cyclisation, in the mild conditions, between organic nitriles and the azide anion in the presence of *d*-electron metals.<sup>2</sup> The most important was the yield of the synthesis and the efficient removing of metal (mostly zinc, but also copper) to recover the organic ligand – tetrazole.<sup>3</sup> In our previous work we have shown, that described in the literature methods do not always work as well as described previously.<sup>4</sup> Nowadays, many methods of the synthesis of tetrazoles have been described, most of them were discovered to decrease the cost of the synthesis, decrease the temperature of the reaction (to avoid explosion) and to get the good yield of the synthesis. The use of lithium as a catalyst is an unique achievement,<sup>5</sup> lastly less expensive Fuller's earth was also applied as the catalyst.<sup>6</sup>

The metal complexes themselves were studied relatively late. Most of the papers describe the synthesis and the structure, without analysing other complex physicochemical properties. The structure of the complexes with tetrazole ligands is very important because many of them form very interesting metal-organic frameworks (MOF), 2D and 3D structures which were identified and described.<sup>7</sup> The coordination to the metal centre may also increase tetrazole's thermal stability and its biochemical accessibility, which results in a wider use of tetrazoles. Tetrazoles might be also coordinated to the metal centre either by the reaction of the metal centre with tetrazole ligands, by the presence (very often as the catalyst of the reaction) of metal ions during tetrazole's synthesis or by the reaction of azido complex with organic nitrile.<sup>2,8</sup> The 1H-tetrazoles have a relatively low pKa value, for example for 5-(2-pyridil)-1H-tetrazole pKa = 4.9, thus they coordinate to most of the *d*-electron metals.<sup>9</sup> If the metal is present during the synthesis of the complex, the complex can be isolated and characterised, but very often it is decomposed without the isolation of pure tetrazoles.<sup>3,10</sup>

Very little is known of the reaction's mechanism of the tetrazole's coordination to the metal centre and about the role of metal in the tetrazole's synthesis. Most of the studied tetrazoles are these with the monodentate mode of the coordination, for the MOF synthesis dinitriles with CN groups in *para* or *meta* position are mostly used. The chelate, *N*-*N* donor ligands are relatively less studied. In order to analyse the sequence of ligand donor atoms coordinated to the metal centre, we described here the 5-(2-pyridil)-1H-tetrazole. As a coordination probe, we used tetracyanido complexes of Mo(IV) and W(IV) for which the mechanism and the sequence of the ligand exchange is well known.<sup>11</sup> The 5-(2-pyridil)-1H-tetrazole (pdt) has two nitrogen donor atoms, the tetrazole nitrogen with *pKa* = 4.9 and the pyridine nitrogen with

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<sup>†</sup>Electronic supplementary information (ESI) available: Selected bond lengths and angles for compound 1 and 2. TGA and IR spectra for 1 and 2. CCDC 1523849-1523850. For ESI and crystallographic data in CIF or another electronic format see DOI: 10.1039/x0xx00000x

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pKa = 5.25.<sup>9</sup> Very similar pKa of both nitrogen atoms should result in the formation of two different coordination modes of pdt in formed  $[M(CN)_4O(pdt)]^{2^-}$  (M = Mo or W) ions, as the coordination sphere of metal is not symmetrical. We used the single X-ray crystal structure determination to describe the coordination modes of tetrazoles, but we also presented other physicochemical properties of the isolated complexes.

#### Experimental

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#### Materials and methods

 $K_3Na[Mo(CN)_4O_2] \cdot 6H_2O$  and  $K_3Na[W(CN)_4O_2] \cdot 6H_2O$  were synthesized according to the literature methods.<sup>12</sup> All other chemicals were of analytical grade (Aldrich) and were used as supplied. Microanalyses of carbon, hydrogen and nitrogen were performed using Elementar Vario MICRO Cube elemental analyser. IR spectra were recorded on a Nicolet iS5 FT-IR spectrophotometer. The electronic absorption spectra were recorded on Shimadzu UV-3600 UV-VIS-NIR spectrophotometer equipped with a CPS-240 temperature controller. Diffuse reflectance spectra were measured in BaSO<sub>4</sub> pellets with BaSO<sub>4</sub> as a reference on Shimadzu 2101PC equipped with an ISR-260 integrating sphere attachment. Cyclic voltammetry measurements were carried out in MeCN (acetonitrile) with  $[Bu_4N]PF_6$  (0.1 M) as the supporting electrolyte, using Pt working and counter and Ag/AgCl as reference electrodes on an AUTOLAB/PGSTAT 128 N Potentiostat/Galvanostat.  $E_{1/2}$  values were calculated from the average anodic and cathodic peak potentials,  $E_{1/2} = 0.5(E_a + E_c)$ . The redox potentials were calibrated versus ferrocene (0.440 V versus SHE), which was used as an internal potential standard for measurements in organic solvents to avoid the influence of a liquid junction potential; the final values were reported versus the standard hydrogen electrode (SHE). DTG measurements were performed on a TGA/SDTA 851e Mettler Toledo Microthermogavimeter under Ar atmosphere in the 25-700 °C range with scan speed 10 °C/min.

#### Synthetic procedures

Synthesis of 5-(2-pyridil)-1H-tetrazole (pdt). Tetrazole ligand derived from 2-cyanopyridine was synthesized according to the modified literature method.<sup>13</sup> To a solution of 2-cyanopyridine (2.18 mL, 20 mmol) in DMF (30 mL) NaN<sub>3</sub> (1.47 g, 20 mmol), NH<sub>4</sub>Cl (1.21 g, 20 mmol) and LiCl (0.32 g, 7.5 mmol) were added. The mixture was heated in the oil-bath at 130 °C for 180 minutes. The resulting precipitate was filtered off and washed with water, which caused dissolution of the precipitate. The pH of the filtrate was lowered to 6.5 with hydrochloric acid (4.0 M). Than the solution was extracted 3 times with 20 mL of CHCl<sub>3</sub>. Evaporation of CHCl<sub>3</sub> solution was used as well.

**Synthesis of (PPh<sub>4</sub>)<sub>2</sub>[Mo(CN)<sub>3</sub>O(pdt)]·2H<sub>2</sub>O (1)**. Tetrazole ligand (0.134 g, 1 mmol) was added to K<sub>3</sub>Na[Mo(CN)<sub>4</sub>O<sub>2</sub>]·6H<sub>2</sub>O (0.490 g, 1 mmol), dissolved in the mixture of water (30 mL) and ethanol (10 mL). The pH was lowered to 9.0 with hydrochloric acid (4.0 M). The resulting dark green solution was treated with a solid (PPh<sub>4</sub>)Br (0.5 g, 1 mmol). After one day, the dark green crystals (1) were filtered off, washed with water and dried in the air at the room temperature. Anal. Calcd. for  $C_{57}H_{48}MoN_8O_3P_2$ : C, 64.08; H, 4.70; N, 10.65%. Found: C, 64.95; H, 4.71; N, 10.15%.

**Synthesis of (PPh<sub>4</sub>)<sub>2</sub>[W(CN)<sub>3</sub>O(pdt)]·3H<sub>2</sub>O (2)**. The synthetic procedure was analogous to the **1**, however instead of  $K_3Na[Mo(CN)_4O_2]\cdot 6H_2O$ ,  $K_3Na[W(CN)_4O_2]\cdot 6H_2O$  (0.568 g, 1 mmol) was used. Anal. Calcd. for  $C_{57}H_{48}WN_8O_3P_2$ : C, 60.06; H, 4.33; N, 9.83 %. Found: C, 59.38; H, 4.05; N, 9.65 %.

#### Crystallography

**Crystallographic data collection and structure refinement.** Crystals of **1** and **2** suitable for X-ray analysis were selected from the materials prepared as described in the Synthetic procedures. The crystal data, details of data collection and structure refinement parameters are summarized in the Table 1. Intensity data for **1** and **2** were collected on a Super Nova diffractometer using monochromatic Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å. The positions of all atoms were determined by direct methods. All nonhydrogen atoms were refined anisotropically using weighted full-matrix least-squares on F2. Hydrogens were included in the structure at idealized positions. The structure was solved using SIR-97 and refined by SHELXL-2014 program.<sup>14</sup>

Table 1 Crystal data and structure refinement parameters for 1 and 2.

	1	2
Empirical formula	C <sub>57</sub> H <sub>48</sub> MoN <sub>8</sub> O <sub>3</sub> P <sub>2</sub>	C <sub>57</sub> H <sub>48</sub> WN <sub>8</sub> O <sub>3</sub> P <sub>2</sub>
Formula weight	1050.91	1144.30
Crystal size (mm)	0.20 × 0.20 × 0.10	0.30 × 0.20 × 0.10
Crystal system	Triclinic	triclinic
Space group	PĪ	Pī
a (Å)	13.3538(6)	13.365(5)
b (Å)	13.5304(5)	13.484(5)
c (Å)	16.6261(7)	16.718(5)
α (°)	71.257(4)	70.768(5)
β(°)	88.524(4)	88.204(5)
γ (°)	62.823(4)	63.024(5)
h	-18 to 18	-18 to 18
k	-18 to 18	-18 to 18
T	-22 to 13	-23 to 23
V (Å <sup>3</sup> )	2504.4(2)	2510.1(15)
Z	2	2
т (К)	120(1)	125(3)
D <sub>x</sub> (g/cm <sup>3</sup> )	1.394	1.514
Reflections measured	23371	40286
Independent reflections	12615 [R(int) = 0.0480]	13585 [R(int) = 0.0526]
Goodness-of-fit on $F^2$	1.227	1.198

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Final R indices [I>2sigma(I)]	R1 = 0.1003, wR2 = 0.1828	R1 = 0.0416, wR2 = 0.0784
R indices (all data)	R1 = 0.1398, wR2 = 0.1972	R1 = 0.0556, wR2 = 0.0828

#### **Results and discussion**

**Crystal Structures.** The asymmetric parts of the unit cells of the complexes **1** and **2** with adopted atomic numbering scheme are shown in the Fig. **1**. Both compounds crystallize in triclinic space group P-1 and are isostructural. They have similar stoichiometry, so the asymmetric part of the unit cells is composed of:  $[M(CN)_3O(pdt)]^{2^-}$  anion (where M = Mo for **1** and M = W for **2**) where pdt = 5-(2-pyridil)-1H-tetrazole (Scheme 1), two PPh<sub>4</sub><sup>+</sup> counterions, and additionally two and three water molecules for **1** and **2**, respectively. Selected bond distances and bond angles are listed in the Table S1 (ESI<sup>+</sup>).



**Scheme 1** Structure of 5-(2-pyridil)-1H-tetrazole, hydrogen atoms are omitted for clarity.



**Fig. 1** Single-crystal X-ray structure of  $[Mo(CN)_3O(pdt)]^{2-}$  (top) and  $[W(CN)_3O(pdt)]^{2-}$  (bottom), hydrogen atoms are omitted for clarity.

In both structures, central atom (Mo for 1 and W for 2) shows static disorder and was refined in two complementary components A and B (percentage ratio of A/B = 44/54 for Mo whereas A/B = 88/12 for W). The geometry around Mo (1) and

W (2) complexes resembles slightly distorted octahedral with equatorial plane formed by three cyano (C1, C2, C3) and one nitrogen (N8 pyridine for A and N4 tetrazole for B) atom of bidentate tetrazole (pdt) ligand. In complex 1 two coordination isomers are observed simultaneously in the structure, the cis one for component A: three cyano ligands and nitrogen atom (N8) of pyridine ring are occupying equatorial positions (the O1A-Mo1A-N8 angle is 94.69°), whereas oxo ligand and nitrogen atom from tetrazole ring (N4) are occupying axial positions (the O1A-Mo1A-N4 angle is 165.52°). In the case of component B of 1 the way of the coordination is reversed (isomer trans) with respect to component A (N4 tetrazole at equatorial and N8 pyridine at axial positions). In both isomers of 1 cyano ligands are displaced from the equatorial plane away from the oxo ligand and the average O1-Mo-C angle is 102.92°. It is the first situation in literature where the same ligand has different coordination - in cis and in trans position to oxo ligand in one crystal. The two different coordination modes of tetrazole (cis and trans to M=O bond) seem to be a not a case, as in both Mo and W complexes this phenomenon was found. For both Mo and W tetracyanides, it is well recognized, that ligand trans to M=O bond is substituted at least order of magnitude faster than cyano ligands. Thus, we expected that the tetrazole nitrogen should be found in this position (as this nitrogen is more basic, pKa = 4.9 versus 5.25 for the pyridine nitrogen). The difference in basicity of both nitrogens is not high, which allows both isomers to be formed. It is worth to mention that the ratio of both isomers is different for Mo than for W analogue, which indicates that additional factors must influence the isomers' ratio. This is probably caused by the fact that the rate constant for the ligand substitution for W is a little lower than for Mo tetracyanide, while formation quotient is substantially (order of magnitude) higher for W than for Mo analogue.

In complex **2** the nitrogen atom (N8) of the pyridine ring is in *cis* position to W=O bond (Fig. 1 bottom). The geometry around W atom is listed in the Table S1 (ESI<sup>+</sup>). In **1** the molybdenum atom is located above the square base of the octahedron (0.4465(43) Å for Mo1A and 0.5377(53) Å for Mo1B) formed by equatorial atoms C1, C2A (C2B), C3 and N8 (N4), in direction to the axial oxygen atom O1A (O1B). In case of compound **2** the tungsten W1A atom is located 0.3743(19) Å above the base of polyhedron defined by C1-C2-C3-N8 atoms. Providing analogous value for W1B component is impossible due to the inability to model the disorder of oxo (O1) and cyano (C2) ligands resulting from the low ratio of the complementary disordered component (12%).

An average metal–C distance is 2.193 Å for **1** and 2.157 Å for **2**. These distances are typical for complexes with bidentate *N*,*N*-donating ligands. The metal–Ooxo (the oxo ligand in axial position) bond distance (Mo for **1**: isomer A = 1.698 Å and B = 1.656 Å, W for **2**: A = 1.717 Å) is typical for cyanooxometalates <sup>15</sup> and is significantly closer to the central metal(IV) ion than to four cyano groups. It is worth noticing that metal–Ooxo bond is relatively short and can be treated rather as the triple bond (Mo=O  $\approx$  1.65 Å) according to the Cotton classification.<sup>16</sup> All interatomic bond distances of

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metal(IV) ion=O are comparable with other characterized cyanooxocomplexes of molybdenum(IV) and tungsten(IV) with mono- and bidentate ligands (avg. 1.68 Å).<sup>15</sup>

In both structures the pyridine group of the pdt ligand (atoms C5-C6-C7-C8-C9-N8) forms a plane twisted to the tetrazole plane (C4-N4-N5-N6-N7) by angle 8.79(10)° and 6.63(2)°, for **1** and **2**, respectively. Generally, all atoms of the pdt ligand in both structures are well established, although displacement ellipsoids of atoms C5-C6-C7-C8-C9-N8 of **1** are significantly larger than other atoms in this structure. This shows a quite significant conformational freedom of the ligand resulting from the static disorder of the structure **1**.

Packing analysis of the crystal structures of **1** and **2** at the supramolecular level reveals that the complex molecules are held together by three hydrogen C-H... $\pi$  bondings (Fig. 2 top) and several hydrogen interactions which are summarized in the Table 2. The X-H... $\pi$  contact can be classified by type IV, according to Malone.<sup>17</sup>



**Fig. 2** Intramolecular C-H... $\pi$  interactions (top), the hydrogen bonds with omitted the H atoms that do not participate in the hydrogen bonds (middle) and the hydrogen bonds network with omitted cations and the hydrogen atoms for clarity (bottom) in **1**.

	ππ [Å]	shift [Å]		
1				
Cg1Cg2 [1+x,-1+y,1+z]	3.985(4)	1.688		
Cg2Cg1 [-1+x,1+y,-1+z]	3.984(4)	2.168		
2				
Cg1Cg2 [x,y,1+z]	3.945(3)	2.086		
Cg2Cg1 [x,y,-1+z]	3.945(3)	1.695		

The lattice of water molecules participates in many hydrogen bonds of C—H···O, O—H···O and O—H···N type (Table 3) linking pairs of complex molecules from two separate layers (O2 and O3) (Fig. 2 middle). All these interactions are

responsible for self-assembly of the complex molecules in layers (Fig. 2 bottom) and stabilization of 3D structure. The shortest intermolecular metal...metal distances are 7.372 Å and 7.270 Å for **1** and **2**, respectively. The tetraphenylphosphonium cations propagate along the [100] and [001] directions and are stabilized by  $\pi$ ... $\pi$  stacking. Chains of [PPh<sub>4</sub>]<sup>+</sup> cations related by translation along *b* axis separate layers of [Mo(CN)<sub>3</sub>O(pdt)]<sup>2-</sup> anions parallel to the *ac* plane.

	HCg [Å]	X-HCg [°]	XCg [Å]
	1		
C12-H12Cg2 [-x,1-y,1-z]	2.72	149	3.563(8)
С31-Н31Сg3 [1-х,1-у,1-z]	2.88	131	3.573(7)
C48-H48Cg4 [-x,1-y,1-z]	2.65	150	3.502(7)
	2		
C(12)-H(12)Cg4 [1-x,1-y,1-z]	2.76	145	3.580(4)
C(43)-H(43)Cg3 [1-x,1-y,1-z]	2.84	132	3.552(5)
C(56)-H(56)Cg1 [2-x,1-y,1-z]	2.70	151	3.558(5)

1: Cg1: C16-C17-C18-C19-C20-C21, Cg2: C40-C41-C42-C43-C44-C45, Cg3: C46-C47-C48-C49-C50-C51, Cg4: N4-N5-N6-N7-C4; 2: Cg1: C28-C29-C30-C31-C32-C33, Cg2: C46-C47-C48-C49-C50-C51, Cg3: C10-C11-C12-C13-

2: Cg1: C28-C29-C30-C31-C32-C33, Cg2: C46-C47-C48-C49-C50-C51, Cg3: C10-C11-C12-C13-C14-C15, Cg4: N4-N5-N6-N7-C4

**IR Spectra.** IR spectra of **1** and **2** are presented in the Fig. S1 (ESI<sup>+</sup>). The  $v_{Mo=0}$  and  $v_{W=0}$  band position is observed at 950 and at 948 cm<sup>-1</sup> in **1** and **2** respectively. For [Mo(CN)<sub>3</sub>O(LL- $\kappa^2$ -N,N)]<sup>n-</sup> complexes (where LL = 1,10-phenanthroline, 2,2'-bipyridine,

2-(aminomethyl)pyridine, Schiff base ligands based on 2-acetylpyridine and ethanolamine, 2-acetylpyridine and methylamine or 2-acetylpyridine and butylamine)<sup>18-21</sup> the  $v_{Mo=0}$ band position is observed in the range 958 – 973 cm<sup>-1</sup>. The  $v_{W=O}$  band position in  $\boldsymbol{2}$  is the lowest among all known W(IV) complexes with N,N-donating ligands and it is similar to  $v_{W=O}$ band position in W(IV) complexes with N,O-donating ligands. The complex with tetrazole ligand is placed between  $(PPh_4)_2[W(CN)_3O(pic)]$  and  $(PPh_4)_2[W(CN)_3O(quinal)]$ .<sup>15</sup> In the C=N stretching region, two bands located at 2098 and 2111 cm<sup>-1</sup> for **1** and at 2089 and 2106 cm<sup>-1</sup> for **2** are observed. These bands are connected with stretching vibrations of three cyano ligands. The bands number, as well as bands positions, is characteristic for complexes of this class. In other regions, the bands typical for PPh4<sup>+</sup> cation, water molecules and tetrazole ligand are observed.

**UV-Vis Spectra.** The UV-Vis absorbance spectra in the solid state and in organic solvents of **1** and **2** are presented in the Fig. 3. The bands with the lowest energy are attributed to *d*-*d* transitions and are located in reflectance spectra at 673 nm for **1** and at 599 nm for **2**. They are overlapped with MLCT (metal-to-ligand charge-transfer) transitions, which are located at 472 nm for **1** and 513 nm for **2**, respectively. In the ultraviolet part (at  $\lambda < 360$  nm) of the reflectance and solution spectra of **1** and **2**, the bands are attributed to transitions within the PPh<sub>4</sub><sup>+</sup> cations, tetrazole ligand and charge-transfer transitions between metal (molybdenum or tungsten) and ligands.

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Fig. 3 UV-Vis reflectance spectra of 1 (top) and 2 (bottom) in BaSO<sub>4</sub> after Kubelka-Munk transformation.

For compounds **1** and **2** the solvatochromism of the MLCT transition is observed. In the Fig. 4 the visible part of the spectrum, corrected to the absorbance = 1.0 (for the most intense MLCT band) is presented.



Fig. 4 UV-Vis spectra of 1 (top) and 2 (bottom) in different solvents, spectra were adjusted to A = 1.0 for the most intense MLCT band.

A roughly linear correlation between  $\lambda_{max}$  and the Reichardt parameter ( $E_{T}$ ) is observed for hydroxylic, non-hydroxylic and alkyl halogenated solvents, as presented in the Fig. 5. Table 4 presents band positions of **1** and **2** and  $E_{T}$  parameter for various solvents. Very similar spectral behaviour has also been observed for all other Mo(IV) and W(IV) complexes  $[M(CN)_{3}O(LL)]^{n-}$  (M = Mo, W).<sup>22,23</sup>

**Table 4** Band positions of **1** and **2** and  $E_T$  parameter for various solvents.

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		1	2	
Solvent	E <sub>T</sub> [kcal·mol <sup>-1</sup> ]	λ [nm]	λ [nm]	
CHCl <sub>3</sub>	39.1	445	503	
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	41.9	454	506	_
CH <sub>2</sub> Cl <sub>2</sub>	41.1	454	506	
Me <sub>2</sub> CO	42.2	471	523	
DMF	43.8	472	505	
DMSO	45.0	463	510	
MeCN	46.0	457	503	
iso-PrOH	48.6	447	498	
<i>n</i> -BuOH	50.2	449	495	
EtOH	51.9	437	483	
MeOH	55.5	431	478	



Fig. 5 The correlations of the band position of 1 (top) and 2 (bottom) versus the solvent  $E_T$  parameter for various solvents.

**Cyclic voltammetry measurements.** The results of cyclic voltammetry measurements for **1** and **2** are presented in the Fig. 6. For **1**, at low scan speeds one oxidation and reduction peak 1 is observed at  $E_{1/2} = 0.407V$ . The peak-to-peak separation (at 50 mV/s, 88 mV) indicates the one electron process. The anodic and cathodic peak separation slightly increases with the increasing scan speed, which may indicate that the reversibility of this process is not full. However, the peak separation increase is not as high as it should be for the typical quasi-reversible redox process. The observed peak 1 is connected with oxidation of Mo(IV) to Mo(V), reversibility of this process is rather rare among  $[Mo(CN)_3O(LL)]^{n-}$  type complexes (where LL denote bidentate organic ligand) and only several complexes with such properties were described in literature.<sup>24</sup> Probably, the presence of the tetrazole ring

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stabilizes the high oxidation state of molybdenum, allowing the redox process to be reversible.

The increase of scan speed results in the formation of the new cathodic peak 2 (see Fig. 6 top) at ca. 0.507 V (at 200mV/s). The lack of anodic peak indicates the irreversible oxidation of Mo(V) to Mo(VI), but the very small shift of the peak position versus scan speed suggests that the oxidation process is in fact reversible. Thus the lack of the anodic peak should be interpreted as the reduction of Mo(VI) (after its formation) in chemical reaction following the redox oxidation. Such process is observed for the first time for this class of Mo(IV) complexes, and it seems that the presence of the tetrazole ligand is responsible for the possibility of the observation of Mo(V)/Mo(VI) redox couple. The presence of the peak 2 at high scan speeds may be also responsible for the observed slight anodic and cathodic potential dependence on scan speed.

The assignment of the peaks in **1** are confirmed by the data for complex **2** presented in the Fig. 6 (bottom). The peak 1 can be attributed to W(IV)/W(V) couple, and is observed at  $E_{1/2} = 0.051V$  while cathodic peak 2 is observed at 0.121 V. This is typical for Mo and W cyano complexes which redox potential of W is much lower than this for Mo, for the similar type of complexes. In the contrary to complex **1**, the cathodic peak for W(IV)/W(V) redox couple becomes visible at higher scan speeds, while the second cathodic peak is visible also at low scan speeds. The only slight peaks position dependence on the scan speed indicates that all observed redox processes are reversible. In general, observed cyclic voltammograms for **1** and **2** are similar, also the shift of the peak 2 versus 1 is similar to both salts.



Fig. 6 Cyclic voltammogram of 1 (top) and 2 (bottom) in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, MeCN as electrolyte.

Thermogravimetry measurements. The thermogram of polycrystalline samples of 2 (W) (Fig. S2 bottom, ESI+) shows that dehydration takes place in the one separate step with T<sub>max</sub> = 88  $^{\circ}$ C ( $\Delta$ m found 3,77 %, calculated for two water molecules  $\Delta m = 3,16$  %). Then, the complex is thermally stable up to 200 °C, at which starts the total decomposition of the complex with PPh4<sup>+</sup>, 3CN<sup>-</sup> and the tetrazole's ligand release. Found for this process  $\Delta m = 71,8$  %, calculated  $\Delta m = 72,3$  %. The dehydrated sample was found to be much more thermally stable than other complexes of [M(CN)<sub>3</sub>O(LL)]<sup>n-</sup> type<sup>25</sup> and indicates that the tetrazole ligand is greatly stabilized by its coordination to the tungsten(IV) centre. In the contrary to 2, the molybdenum analogue (Fig. S2 top, ESI+) starts to decompose much more easily. At  $T_{max} = 73$  °C the dehydration, while at  $T_{max}$  = 142  $^{\circ}$ C 3 HCN molecule release is observed. The processes are not well resolved, however calculated for both decomposition  $\Delta m = 10,3$  %, calculated  $\Delta m = 10,8$  %. Almost together with cyano ligands, release of  $PPh_{4}^{+}$  and tetrazole ligand are observed at  $T_{max}$  = 313 °C. The calculated total  $\Delta m$ (for 2 water molecules, 3 HCN, tetrazole and 2  $PPh_4^+$ ) was found as 88,5 %, calculated  $\Delta m$  = this process  $\Delta m$  = 89,2 %. The decomposition temperature was found to be similar to Ni complexes (328 °C) with tetrazoles, claimed as potential energetic materials<sup>26</sup> and much higher than for Cu(II) complexes with 5-(2-pyridil)-1H-tetrazole and its derivatives.<sup>27</sup> All presented data indicate, that tetrazole ligand do not decompose so easily upon the coordination, thus the coordination is an effective method for stabilization of highly energetic molecules of tetrazoles.

#### Conclusions

The first representatives of tetrazole complexes with Mo(IV) and W(IV) were synthesized and characterized. 5-(2-pyridil)-1H-tetrazole coordinates to the metal centre as the bidentate ligand, but due to the low difference in *pKa* of the pyridine and the tetrazole nitrogen, the formation of two isomers, with the pyridine nitrogen in *trans* or *cis* position to the M=O bond, is observed. This phenomenon could not be observed for symmetric complexes, where *cis* and *trans* position cannot be distinguished. The most surprising was the finding, that *cis* and *trans* isomers coexists in the single crystal, both for Mo and W analogues, forming chains of alternately *cis* and *trans* isomers.

The coordination of the tetrazole to the metal centre resulted in the increase of the thermal stability. This is not a common effect, as for Cu complexes of 5-(2-pyridil)-1H-tetrazole the temperature of the decomposition is ca. 100 °C lower than for Mo(IV) and W(IV) complexes,<sup>27</sup> described complexes could be rather compared with Ni ones, still attributed to the potentially high energetic materials.<sup>26</sup> Moreover, the cyclic voltammetry measurements indicate the possibility of the isolation of Mo(V) and W(V) analogues, probably the tetrazole ring stabilizes the high oxidation state of the metal centre. The strong solvatochromism of MLCT transition, as well as other described properties, make

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described in the paper complexes promising materials for further applications.

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further applications.

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