#### Accepted Manuscript

Synthesis, structure and properties of oxocyanido W(IV) complexes with substituted salicylaldimines of 2-aminoethanol compared to Mo(IV) analogues

Monika Tomecka, Janusz Szklarzewicz, Anna Jurowska, Andrzej Wojtczak

PII:	S0277-5387(14)00381-7
DOI:	http://dx.doi.org/10.1016/j.poly.2014.05.064
Reference:	POLY 10779
To appear in:	Polyhedron
Received Date:	14 April 2014
Accepted Date:	25 May 2014



Please cite this article as: M. Tomecka, J. Szklarzewicz, A. Jurowska, A. Wojtczak, Synthesis, structure and properties of oxocyanido W(IV) complexes with substituted salicylaldimines of 2-aminoethanol compared to Mo(IV) analogues, *Polyhedron* (2014), doi: http://dx.doi.org/10.1016/j.poly.2014.05.064

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Synthesis, structure and properties of oxocyanido W(IV) complexes with substituted salicylaldimines of 2-aminoethanol compared to Mo(IV) analogues.

Monika Tomecka<sup>a</sup>, Janusz Szklarzewicz<sup>a</sup>\*, Anna Jurowska<sup>a</sup> and Andrzej Wojtczak<sup>b</sup>. <sup>a</sup>Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland <sup>b</sup>Faculty of Chemistry, Nicolaus Copernicus University, Gagarnia 7, Toruń, Poland

\*Corresponding author. Tel.: +48 12 6632231; fax: +48 12 6340515. E-mail addresses: szklarze@chemia.uj.edu.pl, janusz.szklarzewicz@uj.edu.pl (J. Szklarzewicz).

#### Abstract

A series of W(IV) complexes with 2-aminoethanol and 5-bromo-, 5-chloro-, 5-methoxy-, 3,5 - dichloro-substituted salicylaldehydes is described. The complexes were isolated and characterized by elemental analysis, IR and UV–Vis spectroscopy as well as cyclic voltammetry. The single crystal X-ray analysis of salt (PPh<sub>4</sub>)<sub>2</sub>[W(CN)<sub>3</sub>O(metsal)]·5H<sub>2</sub>O (where metsal= Schiff bases formed in situ in the reaction of aminoethanol and 5-methoxysalicylaldehyde) indicate a distorted octahedral geometry of the anions with Hmetsal as N,O-donating ligand. The isolated salts of W(IV) are compared to Mo(IV) analogs.

Keywords: Tungsten; Schiff bases; Complexes; Salicylaldehyde; X-ray structure

#### 1. Introduction

The chemistry of metals on low oxidation state has a long and noble history. The stabilization of low oxidation state generally can be achieved by using stabilizing ligands as CO or CN<sup>-</sup> ions. The cyano complexes, soluble in polar solvents (contrary to carbonyl complexes) and stable in solution are thus widely used in molecular magnets synthesis [1]. The advantage of CN ligands is that they can form cyano bridges between metal centers. This type of investigations base mainly on  $[M(CN)_8]^{n-}$  ions (where M = Mo or W, n = 3 or 4), the knowledge about other, lower cyano systems is far more modest [2]. This is mainly caused by lower stability of complexes in solution, thus the synthetic procedure is more complicated. On the other hand, chemistry of lower cyano complexes of Mo(IV) and W(IV) is far more interesting. This includes ligand substitution reaction [3], ligand activation [4], synthesis of new organic molecules [4], activation of small molecules (as O<sub>2</sub>) [5] and in catalytic processes [6]. The very rare advantage of tetracyano complexes, of these two metals, is unique reaction mechanism. The stable octahedral geometry of metal and preserved, in all reaction studies till now, position of remaining cyano ligands versus M=O bond gave possibility of reaction mechanism

study, basing only on crystal structure measurements, especially with chelate ligands [7]. As in  $[M(CN)_4O(L)]^{n-}$  ions (L = OH, H<sub>2</sub>O, n = 3 or 4) ligand L, being always in *trans* position to M=O bond, is first substituted [3]. Crystal structure of formed in reaction  $[M(CN)_3O(LL)]^{m-}$  ions (where LL denotes a bidentate ligand, m = 1 or 2), can show in what sequence ligand LL is coordinated. This can be well seen where LL ligand is not very stable in synthetic conditions (as in case of Schiff base ligands) and is in equilibrium with its components (for LL = Schiff base, amines and aldehydes or ketones) [7]. This gave the unique possibility to study the behavior of ligands (such as Schiff bases) and to transfer this knowledge to complexes with other metal centers.

It is known, that octa-, penta-, tetra- and tricyano complexes of Mo(IV) and W(IV) are isostructural within each listed class [8,9]. In last decade, the very interesting role of tungsten complexes in redox processes, syntheses of new organic molecules in mild and environmentally friendly conditions were indicated [5b]. On the other hand, number of isolated new complexes dramatically decreased, mainly due to synthetic problems. Tungsten is much easier to be oxidized and requires lower synthetic pH (7.5 compared to ca. 9 for Mo analogues) at which many ligands are protonated [11, 12]. Moreover, solutions of formed salts are unstable and relatively fast decomposition with metal oxidation to W(VI) is observed. All this lower the reaction yield, this is especially well seen where Schiff bases as ligands are used.

In the presented paper we describe the synthesis of four complexes of W(IV) with Schiff bases composed of 2-aminoethanol and substituted salicylaldehydes. Ligands were chosen, to get complexes being analogues of described earlier by us Mo(IV) salts [10]. The synthetic procedure was modified, compared to molybdenum salts, to decrease the reaction time and allow the isolation of products as fast as possible to increase the product yield. Due to instability of salts in solution, it was not possible to recrystallize product to get good crystals for X-ray study. Only in one case crystals were suitable for single crystal measurements. The isolated salts are characterized by physicochemical measurements and compared to Mo(IV) analogs.

#### 2. Materials and methods

 $K_3Na[W(CN)_4O_2]\cdot 6H_2O$  was synthesized according to the literature method [9]. All other chemicals were of analytical grade (Aldrich) and were used as supplied. Microanalyses of carbon, hydrogen and nitrogen were performed using a Vario Micro Cube elemental analyzer. The IR spectra were recorded on a Nicolet iS5 FT-IR spectrophotometer. Electronic absorption spectra were measured with a Shimadzu UV–Vis-NIR UV-3600 spectrophotometer. Diffuse reflectance spectra were measured in BaSO<sub>4</sub> pellets with BaSO<sub>4</sub> as a reference using a Shimadzu UV-3600 equipped with an ISR-3100 attachment. Cyclic voltammetry measurements were carried out in DMSO (dimethyl sulfoxide) with [Bu<sub>4</sub>N]PF<sub>6</sub> (0.10 M) as the supporting electrolyte, using Pt working and counter and Ag/AgCl as reference electrodes on AUTOLAB/PGSTAT 128 N Potentiostat/Galvanostat.  $E_{1/2}$  values

were calculated from the average anodic and cathodic peak potentials,  $E_{1/2} = 0.5(Ea + Ec)$ . The redox potentials were calibrated versus ferrocene (0.440 V versus SHE), which was used as the internal potential standard for measurements in organic solvents to avoid the influence of a liquid junction potential; the final values are reported versus the standard hydrogen electrode (SHE). The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE II 500 spectrometer. All spectra were measured immediately after dissolution in DMSO-d<sub>6</sub>.

The ligands used in the synthesis are presented in Fig. 1. They were synthesized in situ, by the reaction of the appropriate substituted salicylaldehydes and aminoethanol. The formed Schiff bases were denoted as Hbrsal, Hclsal, Hmetsal and Hdclsal for 5-bromo-, 5-chloro-, 5-methoxy- and 3,5-dichlorosalicylaldehyde, respectively.



Figure 1. The structure of organic ligands in 1-4 complexes.

#### 2.1. Synthesis of $(PPh_4)_2[W(CN)_3O(clsal)] \cdot 3H_2O(1)$

5-chlorosalicylaldehyde (0.165 g; 1 mmol) and 2-aminoethanol (0.07 ml; 1.2 mmol) were dissolved in ethanol (10 ml) and refluxed for 10 minutes. Then, the solution of  $K_3Na[W(CN)_4O_2]\cdot 6H_2O$  (0.58g; 1 mmol) in 20 ml water and 2-aminoethanol (0.4 ml) were added. The mixture was refluxed for 5 minutes. Afterwards, tetraphenylphosphonium chloride (0.7412 g; 2 mmol) was added and reflux was continued for 10 min. Next, 10 ml of water was added and ethanol was partially evaporated to the start of crystallization. The violet product was filtered off, washed with water and dried in air at room temperature. Yield: 0.4950 g (40%). MW: 1209.34. *Anal.* Calcd. for  $C_{60}H_{55}CIN_4O_6P_2W$ : C, 59.6; H, 4.58; N, 4.63%. Found: C, 60.1; H, 4.54; N, 4.63%. <sup>1</sup>H NMR (500 MHz, DMSO-d\_6, 298 K):  $\delta$  (ppm) 7.98 – 7.71 (m, 35H), 7.18 (s, 1H), 7.18 (s, 1H), 7.01 (d, J = 2.8 Hz, 1H), 6.55 (dd, J = 8.8, 2.8 Hz, 1H), 6.35 (d, J = 8.8 Hz, 1H), 4.27 – 4.13 (m, 3H), 4.08 (t, J = 6.0 Hz, 1H)

2H). <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>, 298 K): δ (ppm) 163.58, 155.90, 155.45, 155.04, 135.11, 134.34, 134.26, 132.69, 130.97, 130.26, 130.16, 119.67, 119.32, 117.77, 117.06, 114.88, 70.14, 62.43.

2.2. Synthesis of  $(PPh_4)_2[W(CN)_3O(brsal)] \cdot 2H_2O(2)$ 

5-bromosalicylaldehyde (0.2013 g; 1 mmol) and 2-aminoethanol (0.060 ml; 1 mmol) were dissolved in ethanol (15 ml) and refluxed for 15 minutes. Afterwards, the solution of  $K_3Na[W(CN)_4O_2]\cdot 6H_2O$  (0.5706 g; 1 mmol) in 37 ml water was added. The mixture changed colour from yellow to dark green. The pH of the solution was lowered with 6M HCl to ca 8.5 and reflux was continued for 20 minutes. Thereafter, the solution of tetraphenylphosphonium chloride (0.7500 g; 2 mmol) in 37 ml water was added. The resulting dark green crystals were filtered off and dried in air at room temperature. Yield: 0.4746 g (38%). MW: 1235.78. *Anal.* Calcd. for  $C_{60}H_{53}BrN_4O_5P_2W$ : C, 58.3; H, 4.32; N, 4.53%. Found: C, 58.4; H, 4.19; N, 4.48%. <sup>1</sup>H NMR (500 MHz, DMSO-d\_6, 298 K):  $\delta$  (ppm) 8.00 – 7.67 (m, 45H), 7.17 (d, J = 10.6 Hz, 1H), 7.13 (d, J = 2.7 Hz, 1H), 6.66 (dd, J = 8.8, 2.7 Hz, 1H), 6.32 (d, J = 8.8 Hz, 1H), 4.19 (s, 3H), 4.09 (t, J = 5.8 Hz, 2H). <sup>13</sup>C NMR (126 MHz, DMSO-d\_6, 298 K):  $\delta$  (ppm) 164.36, 156.22, 155.84, 135.53, 134.76, 134.68, 130.68, 130.58, 120.97, 120.30, 118.19, 117.48, 70.55, 62.84.

#### 2.3. Synthesis of $(PPh_4)_2[W(CN)_3O(metsal)] \cdot 5H_2O(3)$

The synthetic procedure was analogous to the **1**, however 5-metoxysalicylaldehyde (0.15 ml; 1.2 mmol), 2-aminoethanol (0.075 ml; 1.25 mmol), K<sub>3</sub>Na[W(CN)<sub>4</sub>O<sub>2</sub>]·6H<sub>2</sub>O (0.6012 g; 0.95 mmol) and tetraphenylphosphonium chloride (0.7412 g; 2 mmol) were used. Yield: 0.5422 g (41%). MW: 1240.93. *Anal.* Calcd. for C<sub>61</sub>H<sub>62</sub>N<sub>4</sub>O<sub>9</sub>P<sub>2</sub>W: C, 59.0; H, 5.04; N, 4.51%. Found: C, 58.6; H, 4.95; N, 4.43%. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, 298 K):  $\delta$  (ppm) 8.00 – 7.63 (m, 59H), 7.15 (s, 1H), 7.00 (d, J = 2.7 Hz, 1H), 6.73 (d, J = 2.7 Hz, 1H), 4.29 (t, J = 5.9 Hz, 1H), 4.24 – 4.04 (m, 4H). <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>, 298 K):  $\delta$  (ppm) 159.35, 155.72, 155.52, 135.25, 134.50, 134.42, 131.64, 130.42, 130.32, 129.99, 121.62, 120.34, 117.93, 117.22, 114.13, 70.28, 62.58.

#### 2.4. Synthesis of $(PPh_4)_2[W(CN)_3O(dclsal)] \cdot H_2O(4)$

The synthetic procedure was analogous to the **2**, however 3,5-dichlorosalicylaldehyde (0.1913 g; 1 mmol), 2-aminoethanol (0.060 ml; 1 mmol), K<sub>3</sub>Na[W(CN)<sub>4</sub>O<sub>2</sub>]·6H<sub>2</sub>O (0.5684 g; 1 mmol) and the solution of tetraphenylphosphonium chloride (0.7592 g; 2 mmol) in 42 ml water were used. Yield: 0.2165 g (18%). MW: 1164.69. *Anal.* Calcd. for C<sub>58</sub>H<sub>45</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>4</sub>P<sub>2</sub>W: C, 59.8; H, 3.89; N, 3.61%. Found: C, 60.0; H, 4.22; N, 3.82%. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, 298 K):  $\delta$  (ppm) 7.93 – 7.64 (m, 46H), 7.23 (s, 1H), 6.58 (s, 1H), 6.31 (s, 2H), 4.26 – 3.98 (m, 5H), 3.61 (d, J = 10.4 Hz, 3H), 3.53 (s,

1H). <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>, 298 K): δ (ppm) 135.26, 134.51, 134.43, 130.42, 130.32, 117.94, 117.23, 70.28, 62.63, 55.36.

#### 2.5. Crystallographic data collection and structure refinement

Crystals of **3** suitable for X-ray analysis were selected from the materials prepared as described in section 2.3. The crystal data, details of data collection and structure refinement parameters are summarized in Table 1. Intensity data for **3** were collected on a Oxford Sapphire CCD diffractometer using graphite monochromated Mo K $\alpha$  radiation,  $\lambda = 0.71069$  Å. Structure **3** was solved by direct methods and refined using full-matrix least-squares on F<sup>2</sup> with SHELX97 program package [14]. Hydrogen atoms were located from the electron density maps and constrained during refinement.

(3		
Empirical formula	C61 H62 N4 O9 P2 W	
Formula weight	1240.94	
Temperature; K	293(2)	
Wavelength; Å	0.71073	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions; Å, deg	a = 12.1325(3)	
	b = 14.1644(4)	
	c = 18.3487(6)	
	alpha = 69.234(3)	
	beta = 75.813(3)	
	gamma = 83.698(2)	
Volume; Å <sup>3</sup>	2857.53(14)	
Z, Calculated density; Mg/m <sup>3</sup>	2, 1.442	
Absorption coefficient; mm <sup>-1</sup>	2.137	
F(000)	1264	
Crystal size; mm	0.34 x 0.10 x 0.06	
Theta range for data collection; deg.	2.26 to 28.15	
Limiting indices	-15<=h<=14, -18<=k<=12, -22<=l<=24	
Reflections collected / unique	19284 / 12128 [R(int) = 0.0411]	
Completeness to theta	25.00 99.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.8884 and 0.5294	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	12128 / 0 / 694	
Goodness-of-fit on F <sup>2</sup>	0.824	
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.0513	
R indices (all data)	R1 = 0.0679, wR2 = 0.0553	
Largest diff. peak and hole; e.A <sup>-3</sup>	0.664 and -0.790	

Table 1. Crystal data and structure refinement parameters for 3.

<sup>3.</sup> Results and Discussion

The reaction of Schiff bases formed in situ from substituted salicylaldehydes and 2aminoethanol with K<sub>3</sub>Na[W(CN)<sub>4</sub>O<sub>2</sub>]·6H<sub>2</sub>O in appropriate pH conditions results in formation of dark green solution. The colour change is typical for formation of [W(CN)<sub>3</sub>O(LL)]<sup>n-</sup> ions. The complexes were isolated as theirs tetraphenylphosphonium salts. Due to instability of reaction mixtures and fast fading of solution colour [connected with oxidation of W(IV) to W(VI)], synthetic procedure was repeated several times to find best conditions and higher yield of product. Still, the reaction yields are lower than 50%, for complexes 3 and 4 we have to use excess of 2-aminoethanol to get the products at all. In case of salt 4 even so only salicylaldehyde alone coordinates to tungsten centre, as proved also by NMR spectra (see the supporting information Figs. S1 - S8) by the lack of the C=N (imine) shifts (observed in 1 -3 at 159-164 ppm) and lack of aliphatic carbons (in <sup>13</sup>C NMR) and hydrogens (in <sup>1</sup>H NMR). It was also found, that it is impossible (at least in our study), to recrystallize the complexes in all solvents studied by us and even in anaerobic conditions, without complex decomposition. This causes that in NMR spectra peaks attributed to complexes and to its decomposition products are observed, even measured prior to complex dissolution. Thus the number of hydrogens can be only roughly correlated with the complex formula. Only in case of complex  $\mathbf{3}$  we got crystals suitable for X-ray single crystal study from the mother liquor. The compounds are diamagnetic, soluble in polar organic solvents and almost insoluble in water and non-polar solvents.

#### 3.1. Crystal structure

The selected bond lengths and angles for **3** are listed in Table 2 and the anion structure is presented in Fig.2. The crystal structure of **3** contains  $[W(CN)_3O(metsal)]^{2-}$  anion, two PPh<sub>4</sub><sup>+</sup> cations and five water molecules. The Schiff base coordinates as a bidentate ligand to afford a distorted octahedral geometry, with three cyano ligands and nitrogen atom of organic ligand (N1) in equatorial positions, as well as oxo ligand and phenolic oxygen (O1) occupying axial positions.

Bond angles, such as C13-W1-N1, O4-W1-O1 (178.3 and 167.8° respectively), show significant distortion of the octahedron. This type of deformation is observed for all Mo(IV) and W(IV) complexes of the  $[M(CN)_3O(LL)]^{n-}$  (n = 1 or 2) type known until now [3]. In the complex **3** shorter bond lengths between metal and carbon of cyano ligands (2.146, 2.141 and 2.177Å) than in the analogous Mo(IV) complex (2.162, 2.207 and 2.201Å respectively) are observed. The distance between metal and nitrogen atom of the organic ligand is also shorter in the obtained compound than in the Mo(IV) complex (2.166Å for **3** and 2.198Å for Mo analogue).

The crystal packing of complex 3 is shown in Fig.3. The figure shows, that each layer of anions is separated by a layer of cations. The crystal packing is the same as for the analogous Mo(IV) complex.

The anions are bonded by a network of hydrogen bonds. All water molecules, cyanido ligands and O3 molecules are involved in a network of hydrogen bonds, presented in Fig.4. Two adjacent anions are linked by hydrogen bonds N3-O4-W-O4-W-N3. The distances between the anions in complex W(IV) are larger than in the Mo(IV) complex and this is probably the reason for such large differences in the lengths of metal-carbon in these two complexes.

The O4 oxygen does not form hydrogen bonds with the water molecules. However, the distance between O4 and oxygen atom of the methoxy group of the adjacent ligand is 4.495Å, while in the complex of Mo(IV) - 4.521Å. The interaction between the two oxygen atoms may cause a slight increase W=O bond relative to the Mo=O bond (1.707Å and 1.695Å respectively).

-		
(3)		
Bond lengths		
W1=O4	1.707(2)	
W-O1	2.056(2)	
W-N1	2.166(2)	
W-C13	2.146(3)	
W-C12	2.141(6)	
W-C11	2.177(6)	
C13-N4	1.157(4)	
C12-N3	1.146(7)	
C11-N2	1.152(8)	
Bond angles		
O4-W1-O1	178.3(1)	
C13-W1-N1	167.8(1)	
C12-W1-C11	169.0(2)	
N1-W1-O1	82.6(1)	
N1-W1-O4	95.8(1)	
O4-W1-C13	96.1(1)	
C12-W1-N1	88.4(1)	
C11-W1-N1	89.7(1)	
C13-W1-O1	85.6(1)	
C12-W1-O1	84.4(1)	
C11-W1-O1	84.6(1)	

**Table 2.** Selected bond lengths [Å] and angles [°] for 3.



Figure 2. Structure of the  $[W(CN)_3O(metsal)]^{2-}$  ion in 3 with the atom labelling scheme and 50% displacement ellipsoids.





Figure 3. Crystal packing in 3. The hydrogen atoms were omitted for clarity.



Figure 4. The hydrogen bonds network in 3. The cations were omitted for clarity.

#### 3.2. IR spectra

The IR spectra of all complexes are presented in Figs 5 and 6. For  $[M(CN)_3O(LL)]^{n-}$  type complexes (M = Mo or W), the most interesting are bands connected with M=O and C=N vibrations. They are sensitive to the type of donating atoms in LL and symmetry. The v<sub>W=O</sub> bands for salts 1-4 are observed at 930, 928, 926 and 933cm<sup>-1</sup> respectively and in general the energy of v<sub>W=O</sub> bands for

complexes **1**, **2**, **3** and **4** are lower than for complexes described in literature. For example, in complexes with N,O-donating ligands:  $(PPh_4)_2[W(CN)_3O(pic)] \cdot 4H_2O$  [15] (pic= picolinate anion) or  $(PPh_4)_2[W(CN)_3O(ensal)] \cdot 5.5H_2O$  [16] (ensal= N-salicylideneethylenediaminate) these bands are observed at 948 and 936 cm<sup>-1</sup>, respectively. For the complex **4**, with O,O-donating ligand, energy of  $v_{W=O}$  band is also lower than band's energy of the only one known complex of that type,  $(PPh_4)_2[W(CN)_3O(acac)] \cdot 3H_2O$  (Hacac= acetyloacetone) [3]. Substituents on the salicylaldehyde can be arranged in salts 1-4 in order of increasing energy of W=O band: 1,2-dichloro-> chloro->bromo->methoxy-. Thus the 1,2-dichloro- substituent gave the weakest, while the methoxy- the strongest Schiff base ligand bonded to tungsten. This sequence is different from the isostructural Mo(IV) complexes, where the complex with 5-chlorosalicylaldehyde has lower band energy than the complex with 5-bromosalicylaldehyde [10]. The Hammet constants for chloro-, bromo- and methoxy-substituents are 0.23, 0.23 and -0.17 respectively [13]. The imine  $v_{C=N}$  bands are observed in the range 1500-1600 cm<sup>-1</sup> in all spectra, except the spectrum of the complex **4**. The presence of imine bonds confirms the Schiff bases formation.

In the upper right corners of Fig. 5 and 6 the  $v_{C=N}$  bands are presented. Two bands in this region are observed for all salts studied, the lowest energies are observed for the complex with methoxy-substituent **3** (2076 and 2099 cm<sup>-1</sup>), for salts **1**, **2** and **4** at 2087 and 2108; 2092 and 2106 and at 2089 and 2108 cm<sup>-1</sup> respectively. Presence of two bands in this region, with higher intensity of lower energy band is typical for all  $[M(CN)_3O(LL)]^{n-}$  type complexes. Other visible bands come mainly from PPh<sub>4</sub><sup>+</sup> cation, water of hydration and the Schiff base.

C



**Figure 5.** IR spectra of **1** and **2** (dotted line). The upper right corner represents the 2020-2160 cm<sup>-1</sup> parts of the spectra.



Figure 6. IR spectra of 3 and 4 (dotted line). The upper right corner represents the 2020-2160  $\text{cm}^{-1}$  parts of the spectra.

#### 3.3. UV-VIS spectra

The reflectance electronic spectra in the UV-VIS range for all obtained complexes are presented in Fig.7. The lowest energy bands are in the range 600-700 nm and can be attributed to d-d transitions. The d-d transitions are overlapped with MLCT (metal-to-ligand charge-transfer) transitions, which are located at ca 500 nm. Other bands in the ultraviolet range are derived from overlapping bands of organic ligands with bands of LMCT (ligand-metal charge-transfer) transitions of tungsten anion.

The solution UV-VIS spectra were measured in a series of organic solvents. As example, the spectra of all obtained complexes in DMSO were presented in Fig. 8 and indicate a close similarity of observed transitions. The MLCT bands are the most intense and are strongly solvatochromic, which was illustrated for compound 1 in Fig. 9. Positions of this bands are the same for the complexes 1, 2 (511 nm), for complex 3 is shifted to the lower wavelength (502 nm), and band for complex with dichlorosalicylaldehyde has a much lower energy (520 nm) than the other. For the described substituents, position of MLCT bands increases in order: methoxy- < chloro- = bromo- < 1,2-dichloro. Bands at *ca* 650 nm have lower intensity in solvents than in the solid state, which is in agreement with their *d-d* character. These bands are also solvent sensitive, which is caused by overlapping of the MLCT bands on *d-d* transitions, which changes the positions of maximum as MLCT bands shifts and increases intensity of the d-d bands. Similar effect was observed for other complexes of [M(CN)<sub>3</sub>O(LL)] type (M = Mo or W) [17].



Figure 7. UV-vis reflectance spectra of 1, 3 (solid line) and 2, 4 (dotted line) in  $BaSO_4$  after Kubelka-Munk transformation.



Figure 8. UV-vis spectra of 1, 3 (solid line) and 2, 4 (dotted line) in DMSO; T=298 K, d= 1 cm.

To study the specific solvent effects on MLCT transitions, plots of MLCT energy versus Rechardt  $E_T$  solvent parameter are presented in Fig. 10 [18]. Plots show specific effects of solvents, which can be divided in three groups: chloroalkanes, hydroxylic and non-hydroxylic solvents. Such behaviour is the result of different interaction of solvent molecules with oxo, cyano and organic ligand. It can be easily seen (Fig. 10) that halogen- substituted ligands show very similar behaviour, while the methoxy (complex 3) shows different interaction, especially with chloroalkanes.



Figure 9. The electronic spectra of 1 in different solvents. Qualitative spectra normalized for absorbance = 1 for the most intense CT band; T=298 K, d=1 cm.



Figure 10. The MLCT band position versus the Reichardt  $E_T$  parameter for complexes 1-4.

Obtained complexes are unstable in most organic solvents. The investigated compounds are most stable in water. Spectral changes over time for complexes 1-4 in ethanol are shown in Fig. 11. For all compounds, decrease of d-d bands and MLCT bands are observed. In ultraviolet parts, changes of spectra are more complicated. For complexes 1, 2 and 4 disappearance of bands at ca 360 nm and appearance of bands at 390 nm are observed, connected with the Schiff bases release. For compound 3, intensity of band at 380 nm decreased and the new band at 340 nm formed, derived from the free 5-metoxysalicylaldehyde. This indicates not only the organic ligand release, but also the decomposition of Schiff bases into components. Complex 3 is the least stable (the fastest spectral changes) of 1-4 complexes. This observation, together with the decomposition of Schiff base ligand upon complex decomposition in EtOH is a result of different electron withdrawing properties of 5-substituents (the Hammet constant for methoxy- substituent has a negative value, while for substinuents in 1, 2 and 4 positive).

Fig.11 contains also UV-Vis spectra of analogous Mo(IV) complexes. The observed spectral changes are quite similar and evince the decomposition of molybdenum complexes with Schiff bases release, as in tungsten complexes. Complex **4** is different from the Mo(IV) complex with 3,5-dichlorosalicylaldehyde and 2-aminoethanol. In case of molybdenum complex, Schiff base coordinates while in the complex **4**, only aldehyde coordinates as ligand.



**Figure 11.** UV–Vis spectra of **1**, **2**, **3**, **4** and analogous Mo(IV) [10] complexes (on the right) vs. time in ethanol. T= 298K, d= 1 cm, time intervals 180 s. Arrows indicate the direction of the changes.

#### 3.4. Cyclic voltammetry

The cyclic voltammetry measurements were carried out in acetone, using  $Bu_4NPF_6$  (0.1 M) as an electrolyte. The acetone was used as solvent as slowest spectral changes versus time were observed in this solvent. The cyclic voltammograms for different scan speeds (in the 20 - 1000 mv/s range) are presented in Fig.12 and the redox potentials are listed in Table 3. For each complex the oxidation and reduction peaks are symmetrical, their position is independent on the scan speed and the Ea/Ec peaks separation is close to that expected for the one electron process. All this indicates that  $[W(CN)_3O(LL)]^{2-}$  undergoes the reversible oxidation to  $[W(CN)_3O(LL)]^{-}$ . The redox potentials of salts 1 and 2 are very similar (-0.216 and -0.214 V respectively). The highest value of the redox potential is found for compound 4, with 1,2-dichloro substituted LL ligand. The lowest potential is observed for complex 3. For all obtained compounds the  $E_{1/2}$  values are much higher than for analogous W(IV) -0.726 V complexes with NO donating ligands (-0.418 and vs. Fc/Fc<sup>+</sup> for  $(PPh_4)_2[W(CN)_3O(pic)] \cdot 4H_2O[4a]$  and  $(PPh_4)_2[W(CN)_3O(brmetsb)] \cdot 1.5H_2O[10]$  respectively).



**Figure 12.** Cyclic voltammograms of **1**, **2**, **3** and **4** in DMSO for different scan speeds (20 –1000 mv/s); T=298 K.

Redox potential values are dependent on the electron withdrawing effects of 5-substituent in the salicylaldehyde. For the described substituents,  $E_{1/2}$  values increase in order methoxy- < chloro- < bromo- < 1,2-dichloro. For analogous Mo(IV) complexes with the same substituents in 5 position, the corresponding sequence is methoxy- < bromo- < chloro- [10].

Complex		E <sub>1/2</sub> [V]	Δ <b>Ε</b> [ <b>V</b> ]
$(PPh_4)_2[W(CN)_3O(clsal)]\cdot 3H_2O$	(1)	-0.216	0.103
(PPh <sub>4</sub> ) <sub>2</sub> [W(CN) <sub>3</sub> O(brsal)]·2H <sub>2</sub> O	(2)	-0.214	0.086
$(PPh_4)_2[W(CN)_3O(metsal)]\cdot 5H_2O$	(3)	-0.291	0.081
(PPh <sub>4</sub> ) <sub>2</sub> [W(CN) <sub>3</sub> O(dclsal)]·H <sub>2</sub> O	(4)	-0.164	0.093

**Table 3.** The cyclic voltammetry data for complexes 1-4 in DMSO. The redox potentials are reported vs. Fc/Fc<sup>+</sup>; T= 298 K.

#### 4. Conclusion

The synthesised and characterized tungsten(IV) complexes with Schiff base ligands derived from 2-aminothanol and substituted salicylaldehydes (in 5- position with chloro-, bromo- and methoxy- and in 3,5 position with dichloro substituents) indicate, that small changes in aromatic ring result in the well visible physicochemical changes. This comprises spectral changes (IR and UV-Vis, the latter both in solid and in solution), solutions stability and redox properties. Substituents on the salicylaldehyde can be arranged in salts 1-4 in order of increasing position of W=O band: methoxybromo- < chloro- < 1,2-dichloro. For  $E_{1/2}$  values the sequence is almost the same, with the exception of chloro- and bromo- substituents. Influence of substituents on the physicochemical properties is the same as for analogous molybdenum (IV) complexes, with minor differences in the case of Cl and Br substituents in the 5 position. For compound **3** the crystal structure was determined and differences in the network of hydrogen bonds relative to the analogue Mo(IV) complex were demonstrated. In complex **3** two adjacent anions are linked by hydrogen bonds by two oxygen atoms. In analogous Mo(IV) complex, two nitrogens of cyanido ligands form bridge with one water molecules. This results in significant differences in bond lengths in comparable complexes.

#### Acknowledgment

The research was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (contract no. POIG.02.01.00-12-023/08).

#### Appendix A. Supplementary data

CCDC 990212 contain the supplementary crystallographic data for complex 3. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>.

#### References

- K. Nakagawaa, K. Imotoa, H. Miyaharaa, S. Ohkoshi, Polyhedron, 52 (2013) 424; D. Matoga,
   M. Mikuriya, M. Handa, J. Szklarzewicz, Chem. Lett., 34 (2005) 1550.
- [2] K. S. Lim, Ch. S. Hong, Dalton Trans., 42 (2013) 14941; D.-P. Dong, T. Liu, H. Zheng, L. Zhao, P.-F. Zhuang, Ch. He, Ch.-Y. Duan, Inorg. Chem. Commun., 24 (2012) 153.
- [3] A. Samotus, J. Szklarzewicz, D. Matoga, Bull. Pol. Acad. Sci. Chem., 50 (2002) 145.
- [4]a) J. Szklarzewicz, A. Makuła, D. Matoga, J. Fawcett, Inorg. Chim. Acta., 358 (2005) 1749; b)
  D. Matoga, J. Szklarzewicz, K. Lewiński, Polyhedron, 27 (2008) 2643; c) D. Matoga, J. Szklarzewicz, K. Lewiński, Polyhedron., 29 (2010) 94; d) A. Ryniewicz, M. Tomecka, J. Szklarzewicz, D. Matoga, W. Nitek, Polyhedron, 45 (2012) 229.
- [5] a) J. Szklarzewicz, K. Stadnicka, Inorganica Chimica Acta, 393 (2012) 131; b) J. Szklarzewicz,
   D. Matoga, M. Owcarz, W. Przybylski, D. Yoshioka, M. Mikuriya, Inorg. Chem. Commun., 12 (2009) 819;
- [6] D. Matoga, J. Szklarzewicz, A. Samotus, J. Burgess, J. Fawcett, D.R. Russell, Polyhedron, 19 (2000) 1503; J. Szklarzewicz, D. Matoga, A. Samotus, J. Burgess, J. Fawcett, D. R. Russell, Croatica Chem. Acta, 74 (2001) 529; D. Matoga, J. Szklarzewicz, A. Samotus, K. Lewiński, J. Chem. Soc. Dalton Trans., (2002) 3587.
- [7] J. Szklarzewicz, D. Matoga, A. Kłyś, W. Łasocha, Inorg. Chem., 47 (2008) 5464; P. R. Robinson, E. L. Moorehead, B. J. Weathers, E. A. Ufkes, T. M. Vickrey, G. N. Schrauzer, J. Am. Chem. Soc., 98 (1976) 2815; G. N. Schrauzer, P. R. Robinson, E. L. Moorehead, T. M. Vickrey, J. Am. Chem. Soc., 97 (1975) 7069; E. L. Moorehead, P. R. Robinson, T. M. Vickrey, G. N. Schrauzer, J. Am. Chem. Soc., 98 (1976) 6556; P. R. Robinson, E. L. Moorehead, B. J. Weathers, E. A. Ufkes, T. M. Vickrey, G. N. Schrauzer, J. Am. Chem. Soc., 98 (1976) 6556; P. R. Robinson, E. L. Moorehead, B. J. Weathers, E. A. Ufkes, T. M. Vickrey, G. N. Schrauzer, J. Am. Chem. Soc., 99 (1977) 3657.
- [8] A. Jurowska, J. Szklarzewicz, K. Kurpiewska, M. Tomecka, Polyhedron, (2014), DOI: http://dx.doi.org/10.1016/j.poly.2014.03.021
- [9] A. Roodt, S.S. Basson, J.G. Leipoldt, Polyhedron, 13 (1994) 599.
- [10] J. Szklarzewicz, M. Skaisgirski, P. Paciorek, K. Kurpiewska, P. Zabierowski, M. Radoń, Polyhedron, 68 (2014) 112.
- [11] A. Roodt, J. G. Leipoldt, S. S. Basson, I. M. Potgieter, Transition Met. Chem., 13 (1988) 336.
- [12] A.Kanas, M. Dudek, A. Samotus, Bull. Acad. Polon Sci. Ser. Sci. Chim., 24 (1976) 43.

[13] C. Hansch, A. LEO, R. W. Taft, Chemical Reviews., 91 (1991) 165-195

- [14] G. M. Sheldrick, Acta Crystallogr. Sect. A: Found. Crystallogr. A64 (2008) 112.
- [15] J. Szklarzewicz, A. Mikuła, D. Matoga, J. Fawcett, Inorganica Chimica Acta, 358 (2005) 1749.
- [16] B. Nowicka, A. Samotus, J. Szklarzewicz, F.W. Heinemann, H. Kisch, J. Chem. Soc., Dalton Trans., (1998) 4009.
- [17] A. Al-Alousy, J. Burges, A. Samotus, J. Szklarzewicz, Spectrochemica Acta, vol. 47A, No 8, (1991) 985.
- [18] C. Reichardt, Losungsmitteleffekte in der Organischen Chemie., Verlag Chemie, Weinheim (1968); C. Reichardt and E. Harbuech-Gornert, Liebigs Ann. Chem., 721 (1983).

21



A series of W(IV) Schiff base ligand complexes were obtained in reaction of  $[W(CN)_4O_2]^{4-}$  with 2-aminoethanol and 5-bromo-, 5-chloro-, 5-methoxy-, 3,5 -dichloro-substituted salicylaldehydes. In case of 3,5-dichlorosalicylaldehyde, the complex only with salicylaldehyde was obtained. The salts were isolated and characterized by elemental analysis, IR and UV-Vis spectroscopy and cyclic Acception voltammetry. Results were compared to molybdenum analogues.