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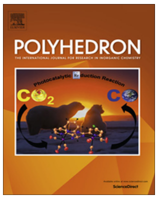

Synthesis, structure and properties of oxocyanido W(IV) complexes with substituted salicylaldimines of 2-aminoethanol compared to Mo(IV) analogs

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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 $(PPh_4)_2[W(CN)_3O(metsal)]\cdot 5H_2O$ (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.

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^- 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 centres. 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_2) [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_2O, $n = 3$ 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 centres.

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 analogs) 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

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complexes being analogs 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 $BaSO_4$ pellets with $BaSO_4$ 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 $[Bu_4N]PF_6$ (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, $E_{1/2} = 0.5(E_a + E_c)$. 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 ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE II 500 spectrometer. All spectra were measured immediately after dissolution in DMSO-d_6.

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.

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 min. Then, the solution of $K_3Na[W(CN)_4O_2]\cdot 6H_2O$ (0.58 g; 1 mmol) in 20 ml water and 2-aminoethanol (0.4 ml) were added. The mixture was refluxed for 5 min. 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.* Calc. for $C_{60}H_{55}ClN_4O_6P_2W$: C, 59.6; H, 4.58; N, 4.63. Found: C, 60.1; H, 4.54; N, 4.63%. ^1H NMR (500 MHz, DMSO-d_6, 298 K): δ (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, 2H). ^{13}C NMR (126 MHz, DMSO-d_6, 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.

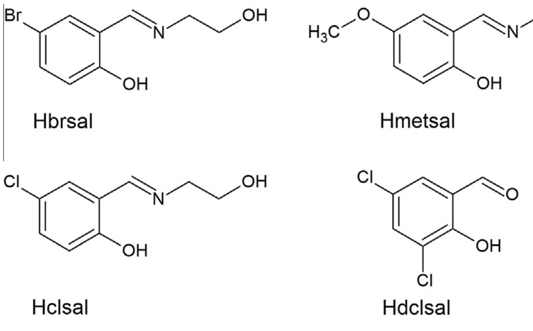

Fig. 1. The structure of organic ligands in **1**–**4** complexes.

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 min. 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 color from yellow to dark green. The pH of the solution was lowered with 6 M HCl to ca 8.5 and reflux was continued for 20 min. 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.* Calc. 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%. ^1H NMR (500 MHz, DMSO-d_6, 298 K): δ (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). ^{13}C NMR (126 MHz, DMSO-d_6, 298 K): δ (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), $K_3Na[W(CN)_4O_2]\cdot 6H_2O$ (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.* Calc. for $C_{61}H_{62}N_4O_9P_2W$: C, 59.0; H, 5.04; N, 4.51. Found: C, 58.6; H, 4.95; N, 4.43%. ^1H NMR (500 MHz, DMSO-d_6, 298 K): δ (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). ^{13}C NMR (126 MHz, DMSO-d_6, 298 K): δ (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), $K_3Na[W(CN)_4O_2]\cdot 6H_2O$ (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.* Calc. for $C_{58}H_{45}Cl_2N_3O_4P_2W$: C, 59.8; H, 3.89; N, 3.61. Found: C, 60.0; H, 4.22; N, 3.82%. ^1H NMR (500 MHz, DMSO-d_6, 298 K): δ (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). ^{13}C NMR (126 MHz, DMSO-d_6, 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,