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New dioxidouranium (VI) and mixed-valence oxidovanadium (IV/V) coordination compounds with N,O-pentadentate ligands obtained from pyridoxal and triethylenetetramine

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ABSTRACT

This work describes the synthesis and structural analysis of the uranium and vanadium complexes $[(UO_2)(C_{22}H_{30}N_6O_4)]\cdot MeOH$ (**1**) and $[(VO)_2(O)(C_{30}H_{36}N_7O_6)]\cdot 3MeOH$ (**2**) with ligands obtained from the condensation of pyridoxal and triethylenetetramine. The probable mechanism for the formation of imidazoline rings in these complexes is described in some details. Finally, electrochemical and UV–Vis studies of the dinuclear vanadium complex were also carried out in order to determine the variation in the oxidation states of the metallic centers (VO^{2+}/VO^{3+}) in DMSO solution.

1. Introduction

There are numerous examples in the literature of organic ligands, which are used as coordinating agents [1,2]; however, there are few examples involving derivatized pyridoxal molecules [3,4]. Therefore, interest in working with pyridoxal type ligands is justified, since it is present in the metabolism of coenzymes of various biosynthetic pathways and regulatory processes. Among these processes, transamination of amino acids is one of the most known [5]. For the cases where pyridoxal and its derivatives act as coordinating agents, there are examples in the literature associated with the synthesis of novel organometallics and even mimics of insulin [6,7].

More specifically, examples involving vanadium and uranium are scarce, even considering that one of the focus of the study of uranium bioinorganic derivatives is related to the understanding of the behavior of this element in living organisms and investigating ways to eliminate the metal through treatment with chelation agents [8]. These studies revealed why the body has difficulty to eliminate uranium [9] and can even cause severe damage to DNA [10] and organs such as the kidneys [9]. In the case of vanadium, there is a beneficial relationship to living organisms, because this element is found in great abundance and variety. It has been identified in terrestrial organisms such as the *Amanita muscaria* mushroom species [11], in enzymatic centers of marine organisms like vanadium-bromoperoxidase [12] and in numerous research projects involving biological applications [13].

In this article we report the synthesis and X-ray structural characterization of novel uranium and vanadium complexes, formed by uranyl or bis-vanadyl units with a Schiff base ligand. The ligand is formed by direct condensation of triethylenetetramine and pyridoxal. We also report the electrochemical characterization of the vanadium complex, and this is an important result in the identification of the redox state of the vanadium centers in the mixed valence complex.

2. Experimental

2.1. X-ray crystallography

Data were collected with a Bruker APEX II CCD area-detector diffractometer and graphite-monochromatized Mo Kα radiation. The structure was solved by direct methods using SHELXS [14]. Sub-

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Table 1
Crystal data and structure refinement for complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{23}H_{34}N_6O_7U$	$C_{33}H_{48}N_7O_{12}V_2$
Formula weight	744.59	836.66
T (K)	273(2)	100(2)
Radiation, λ (Å)	0.71073	0.71073
Crystal system, space group	triclinic, $P\bar{1}$	orthorhombic, $P2_12_12_1$
Unit cell dimensions a, b, c (Å)	$a = 7.165(5)$ $b = 9.434(5)$ $c = 19.693(5)$	$a = 12.447(3)$ $b = 16.867(3)$ $c = 18.688(4)$
α, β, γ (°)	$\alpha = 97.753(5)$ $\beta = 93.019(5)$ $\gamma = 99.422(5)$	$\alpha = 90$ $\beta = 90$ $\gamma = 90$
V (Å^3)	1297.4(12)	3923.4(4)
Z, d_{calc} (g cm^{-3})	2, 1.906	4, 1.416
Absorption coefficient (mm^{-1})	6.310	0.544
F(000)	1196	1748
Crystal size (mm)	0.360 × 0.194 × 0.092	0.458 × 0.386 × 0.227
θ range (°)	2.58–30.53	1.97–25.76
Index ranges	$-10 \leqslant h \leqslant 9$, $-13 \leqslant k \leqslant 13$, $-28 \leqslant l \leqslant 28$	$-15 \leqslant h \leqslant 15$, $-13 \leqslant k \leqslant 20$, $-21 \leqslant l \leqslant 22$
Reflections collected	36456	20637
Reflections unique	7867 [R(int) = 0.0323]	7444 [R(int) = 0.0640]
Completeness to theta maximum	98.9%	98.8%
Absorption correction	gaussian	gaussian
Maximum and minimum transmission	0.560 and 0.239	0.884 and 0.779
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	7867/0/335	7444/0/496
Goodness-of-fit (GOF) on F^2	1.015	1.053
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0253$, $wR_2 = 0.0493$	$R_1 = 0.0795$, $wR_2 = 0.2133$
R indices (all data)	$R_1 = 0.0326$, $wR_2 = 0.0511$	$R_1 = 0.0973$, $wR_2 = 0.2275$
Largest difference in peak and hole (e Å^{-3})	1.220 and −0.699	1.311 and −0.466

sequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinements were carried out with the SHELXL package [14]. All refinements were made by full-matrix least squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions but the atoms (of hydrogens) that are commenting performing special bond were located in the Fourier map. Illustrations of complexes were done using DIAMOND for Windows [14a]. Crystal data and more details of the data collection and refinements of the complexes **1** and **2** are contained in Table 1.

2.2. Instrumentation

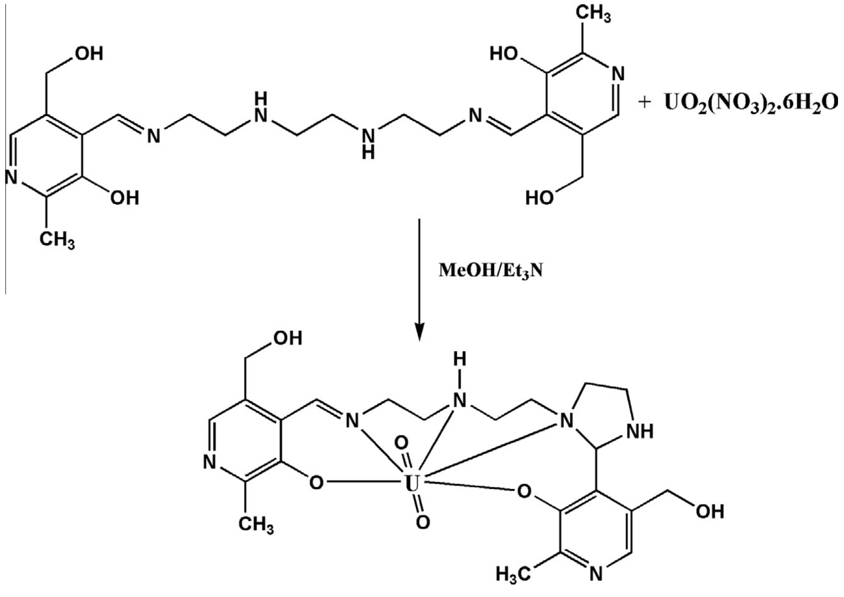
UV–Vis spectra were recorded on a Perkin-Elmer Lambda 191 spectrometer. Cyclic voltammograms were recorded with a Princeton Applied Research (PAR) 273 system at room temperature under argon atmosphere, in dry dimethylsulfoxide (DMSO). Electrochemical grade tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was used as supporting electrolyte. A standard three-electrode system was employed to carry out these experiments: a glassy carbon working electrode; a platinum wire auxiliary electrode and a platinum wire pseudoreference electrode. To monitor the reference electrode, the ferrocenium/ferrocene couple was used as an internal reference ($E_{1/2}$ = 400 mV versus NHE) [15].

All manipulations were conducted by use of standard Ar atmosphere. Elemental analyses for C, H and N were performed at a Shimadzu EA 112 microanalysis instrument. IR spectra were recorded on a Tensor 27 – Bruker spectrometer with KBr pellets in the 4000–400 cm^{-1} range. The syntheses of **1** and **2** are resumed in Schemes 1 and 2.

2.3. Synthetic procedures

2.3.1. Ligand *L1*

Pyridoxal hydrochloride (0.203 g, 1 mmol) was dissolved in 25.0 mL of anhydrous methanol (MeOH) and mixed with 0.056 g (1.0 mmol) of potassium hydroxide (KOH). The white solution was stirred by 10 min under argon atmosphere. To this solution, 0.5 mmol (0.073 g) of triethylenetetramine was suspended and 5.0 mL of methanol (MeOH) was added slowly. Thereafter the mixture was heated in an oil-bath at 50 °C for ~2.0 h. After completion of the reaction, the solvent was evaporated and afforded a yellow precipitate, which was washed with methanol at 5 °C. Properties: light yellow crystals. Melting point: 85–86 °C. The ligand was



Scheme 1. Synthesis of **1**.