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Synthesis and antioxidant activities of oxovanadium(IV) complexes with amino acid ligands

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The vanadium redox behavior is one of the barriers to the development of bioactive agents. Strategies have been developed to synthesize vanadium coordination compounds using antioxidant ligands, such as amino acids, to favor an antioxidant mechanism and, consequently, reduce the production of free radical reactive oxygen species such as superoxide anion $O_2^{\cdot-}$, hydroxyl radical ($OH^{\cdot}$) and hydrogen peroxide (H_2O_2) that can induce DNA damage and oxidative stress in humans [1]. This work aims to synthesize, structurally characterize, and evaluate the antioxidant activity of three vanadium(IV)-amino acid complexes and derivatives of thiosalysilic acid. The complexes were synthesized using sodium thiosalicylate, vanadyl sulfate, and the respective amino acid (alanine, proline, or phenylalanine) (1:1:1) in an aqueous medium, pH adjusted to 7, using a NaOH 0.1 mol L^{-1} solution. The structures of the described compounds, abbreviated as 1a, 1b, and 1c (Table 1) were elucidated by spectroscopic techniques (IFT-IR, UV-Vis, and EPR). The infrared spectroscopy analysis (IFT-IR) showed the V=O stretches (~900-950 cm^{-1}) as well as modifications to the stretches of the ligand elements, confirming coordination via the SNO_2 mode with V(IV) metallic center. The electronic paramagnetic resonance spectroscopy (EPR) of the ^{51}V compounds (I = 7/2) showed the eight-hyperfine lines (g_{iso} = 1.963), confirming the formation of the V(IV)-coordination compounds. The antioxidant activity of these complexes has been investigated in the Cupric Reducing Antioxidant Capacity (CUPRAC) assay using Trolox as a standard, as described by Apak *et al.* [2]. The CUPRAC method is based on the reduction of a cupric neocuproine complex (Cu(II)-Nc) by antioxidants to the yellow-orange colored cuprous chelate (Cu(I)-Nc) [3]. All determinations were carried out at least three times and in triplicate at each separate concentration of the samples to generate consistent data with statistical errors. The compounds screened for antioxidant capacity showed high antioxidant values compared to other vanadium complexes and known antioxidants described in the literature [3,4], as shown in Table 1. This study may support the research on the biologically active vanadium complexes as antioxidants and use some of these compounds in clinical therapy as possible therapeutic agents.

Table 1. Antioxidant capacities of the vanadium-aminoacid compounds (in Trolox® equivalent antioxidant capacity µmol L^{-1}) as measured by CUPRAC assay.

Compounds	µmol TE L^{-1}	mmol TE/g
[VO(Ala)(tiosac)] (1a)	1798,14 ± 15,1	719,26 ± 10,5
[VO(pro)(tiosal)] (1b)	2245,29 ± 10,0	898,11 ± 3,5
[VO(FA)(tiosal)] (1c)	2422,43 ± 11,3	968,97 ± 4,1

*The data are expressed in µmol equivalent Trolox/L and mmol equivalent Trolox/L ± S.E.M.

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