



Donor atom electrochemical contribution to redox potentials of square pyramidal vanadyl complexes



Manolis Vlasίου^a, Chryssoula Drouza^{b,*}, Themistoklis A. Kabanos^{c,**}, Anastasios D. Keramidis^{a,***}

^a Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus

^b Department of Agricultural Sciences, Biotechnology and Food Science, Cyprus University of Technology, Lemesos 3036, Cyprus

^c Department of Chemistry, Section of Inorganic and Analytical Chemistry, University of Ioannina, 45110 Ioannina, Greece

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ABSTRACT

A simple donor atom additivity relationship has been used to calculate the donor atom electrochemical contribution (*DEC*) of the O_{ac} (acetylacetonate-enolic oxygen), O_{Ph} (phenolic oxygen), S_{Ph} (mercaptophenol sulfur), N_{am} (deprotonate amide nitrogen), N_{im} (imine nitrogen) and N_{py} (pyridine nitrogen) to the redox processes of the square pyramidal vanadyl complexes. The study focuses on the amidate vanadyl complexes because of (a) their biological interest and (b) the existence of data from plethora complexes studied in great details. The electrochemical contributions for the vanadyl oxidation and reduction processes increase following the same order, $O_{Ph} \sim O_{ac(enolic)} < S_{Ph} \sim N_{am} < N_{im} < N_{py}$. These values predict the electrochemical potentials of square pyramidal vanadyl complexes with high accuracy. Octahedral complexes with the same equatorial environment show significant shift of the oxidation potentials to lower values. The *DEC* influence to the square pyramidal vanadyls' electrochemical potentials has been evaluated.

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1. Introduction

Vanadium is an important element with biological [1–9], catalytic [10–14] and technological [15–18] properties and applications. The important properties of vanadium in large part are attributed to the stability of the different oxidation states, vanadium(III, IV and V).

Pickett and Pletcher [19] introduced a ligand's additivity rule for predicting successfully the electrochemical potentials of a number of carbonyl complexes. The model was applied in several other cases later [20,21] supporting that in general this model can be used for the prediction of the electrochemical potentials. However, despite the importance of predicting the electrochemistry of vanadium complexes and better understanding of the properties of the donating atoms, the ligand additivity rule hasn't been applied to vanadium compounds. This is mainly because (a) vanadium complexes exhibit different geometries [22], thus it is difficult for common parameters to be applied on complexes of different ligands, (b) lack of large number of complete studied

complexes with similar geometry and (c) the potentials were measured with various references, creating confusion.

In order for us to establish the model for vanadium complexes and to avoid such complications we have selected to study only the square pyramidal vanadyl complexes in organic solvents (mainly CH_3CN). Square pyramidal vanadyl complexes are quite common and there are several well studied examples especially with amidate ligands which are related to proteins. Vanadium is well known for its interaction with proteins [7,23–26] and peptides [27], thus, the exploration of the interaction of vanadium with potential metal ion binding sites on proteins is very important [28]. The high sensitivity of electrochemistry in association with the electrochemical potential predicting model can be used as a tool for the identification of the donor atoms and the structure of vanadium complexes in biomolecules.

Parameterization of the oxidation process of vanadyl electrochemistry has been tried with $[VO(salen)]$ [Fig. 1, $salen^{2-} = N,N'$ -ethylenebis(salicylideneamine)] with different substituents in the aromatic ring [29,30]. In addition, the oxidation potential correlates linearly against Hammett ρ_p [31]. However, these studies are focus only on the correlation of electron density on the metal ion in $[VO(salen)]$ and the oxidation potential but not on the effect of ligands containing different donor atoms.

Herein, we have applied a simple additivity rule on different ligands for predicting the oxidation and reduction potentials of square pyramidal vanadyl complexes. The role of axial substitution has been also

* Corresponding author. Tel.: +357 25002503; fax: +357 25002655.

** Corresponding author. Tel.: +30 2651008415; fax: +30 2651007006.

*** Corresponding author. Tel.: +357 22892764; fax: +357 22895454.

E-mail addresses: chryssoula.drouza@cut.ac.cy (C. Drouza), tkampano@cc.uoi.gr (T.A. Kabanos), akeramid@ucy.ac.cy (A.D. Keramidis).

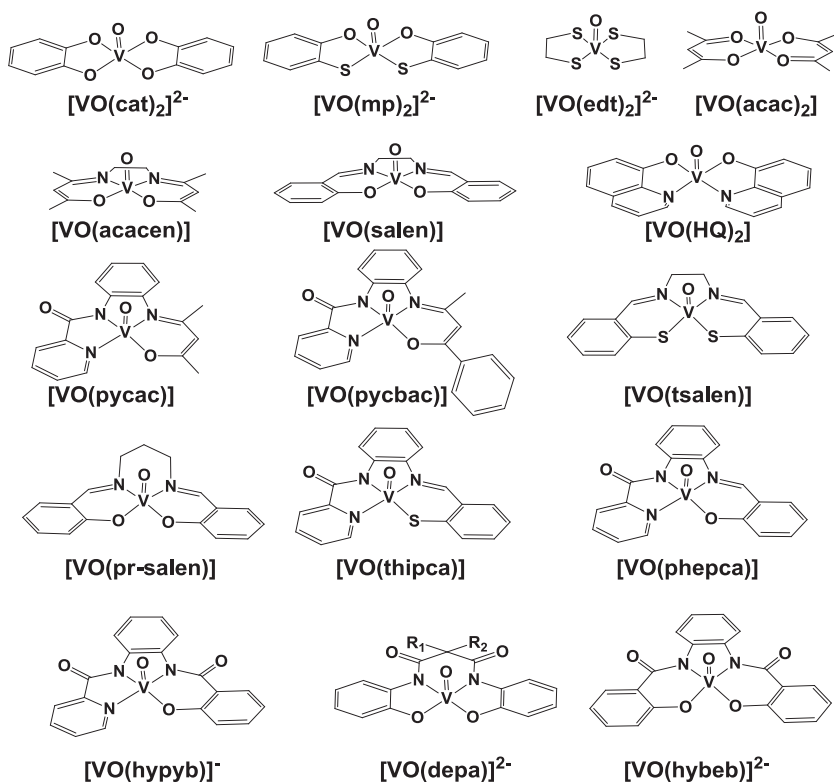


Fig. 1. Complexes referred in this study.

investigated. The contribution of each donor atom in the electrochemical potentials of the molecules is calculated and evaluated.

2. Experimental section

2.1. Synthesis

The $K_2[VO(cat)_2]$ [32], $Na_2[VO(hybeb)]$ [28], $Na[VO(hypyb)]$ [28], $[VO(pycac)]$ [33,34], $[VO(salen)]$ [35] and $[VO(acac)_2]$ [36] (cat^{2-} = catecholate, $hybeb^{4-}$ = 1,2-bis(2-hydroxybenzamido)benzene, $hypyb^{3-}$ = 1-(2-hydroxybenzamido)-2-(2-pyridinecarboxamido)benzene, $pycac^{2-}$ = N-[2-(4-oxopent-2-en-2-ylamino)phenyl]pyridine-2-carboxamide, $acac^-$ = acetylacetonate) were synthesized

according to the literature. The purity of the complexes was confirmed by elemental analysis (microanalyses for C, H, and N were performed by a Euro-Vector EA3000 CHN elemental analyzer).

2.2. Electrochemistry

Cyclic voltammetry (CV) experiments were conducted on an EG&G Princeton Applied Research 273A potentiostat/galvanostat. Electrochemical procedures were performed with a three-electrode configuration: a platinum disk electrode was used as the working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference. The potential of the reference electrode was standardized using ferrocene [0.665 V vs NHE (Normal Hydrogen

Table 1

Experimental (E_{exp}), calculated (E_{calc} Eq. (1)) one electron oxidation and one electron reduction electrochemical potentials (V) vs NHE for square planar complexes with different equatorial environments.

Compounds	$VO^{2+} = VO^{3+} + e^-$		$VO^{2+} + e^- = VO^+$		Equatorial environment of the complexes
	E_{exp}	E_{calc}	E_{exp}	E_{calc}	
$[VO(acacen)]$ [44]	0.54	0.530	-1.83	-1.830	$N_{im2}O_{ac2}$
$[VO(salen)]$ [40]	0.47	0.500	-1.66	-1.660	$N_{im2}O_{Ph2}$
$[VO(phepca)]$ [28]	0.969	0.845	-1.40	-1.358	$N_{am}N_{im}N_{py}O_{Ph}$
$[VO(thipca)]$ [28]	0.91	0.903	-1.21	-1.173	$N_{am}N_{im}N_{py}S_{Ph}$
$[VO(hypyb)]^-$ [28]	0.581	0.579	-1.71	-1.766	$N_{am2}N_{py}O_{Ph}$
$[VO(hybeb)]^{2-}$ [28]	-0.047	-0.032		-2.467	$N_{am2}O_{Ph2}$
$[VO(pycac)]$ [33]	0.82	0.860	-1.51	-1.443	$N_{am}N_{im}N_{py}O_{ac}$
$[VO(pycbac)]$ [34]	0.86	0.860	-1.43	-1.443	$N_{am}N_{im}N_{py}O_{ac}$
$[VO(tsalen)]$ [45]	0.56	0.616	-1.29	-1.290	$N_{im2}S_{Ph2}$
$[VO(mp)_2]^{2-}$ [46]	0.050	-0.0084		-2.510	$O_{Ph2}S_{Ph2}$
$[VO(cat)_2]^{2-}$	-0.070	-0.124		-2.880	O_{Ph4}
$[VO(HQ)_2]$ [47]	1.095	1.098	-1.46	-1.460	$N_{py2}O_{Ph2}$
$[VO(depa)]^{2-}$ [48]	-0.032	-0.032		-2.467	$N_{am2}O_{Ph2}$
$[VO(pr-salen)]$ [49]	0.50	0.500		-1.660	$N_{im2}O_{Ph2}$

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