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Electrochemical and spectral behaviour of binary and mixed-ligand complexes of oxovanadium(IV) with dipicolinic acid and diimines in dimethylsulfoxide

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ABSTRACT

The cyclic voltammetric (CV) studies of five binary oxovanadium (IV) complexes $[VO(diimine)_2]^{2+}$ where diimine = 4,4′-Me_2bipy **A**; 5,5′-Me_2bipy **B**; dmp **C**; bathophen **D**; and bathocuproin **E** and seven mixed-ligand oxovanadium (IV) complexes of dipicolinic acid (DPA) with diimines, [VO(DPA)(diimine)] where diimine = bipy **1**; 4,4′-Me_2bipy **2**; 5,5′-Me_2bipy **3**; phen,**4**; dmp **5**; bathophen **6** and bathocuproin **7** were carried out in dimethyl sulfoxide (DMSO). The reduction of binary $[VO(diimine)_2]^{2+}$ complex (VO^{2+}/V^{3+}) involving bathophen was the easiest while that involving dmp was the most difficult. The electronic spectra of all these binary $[VO(diimine)_2]^{2+}$ complexes in DMSO solution showed a weak broad band in the region 833–736 nm which was assigned to d–d transitions. The mixed-ligand complex involving 5,5′-Me_2bipy was the easiest oxidation and bathophen was the most difficult to oxidize amongst all these complexes in the given medium. The reduction was the easiest in mixed-ligand complex involving bathophen and the most difficult in the case of dmp. The UV–visible spectra of all mixed ligand complexes were also studied in respective medium.

1. Introduction

Vanadium is an important trace transition metal having useful biological activity, especially in insulin-like bio-activity [1–4]. It can help to lower the increased glucose level in the blood of diabetic animals and patients [5]. It also serves as an electron acceptor which could stimulate enzymatic and non-enzymatic oxidation of NADH (β-nicotinamide adenine dinucleotide) and NADPH (β-nicotinamide adenine dinucleotide phosphate) into their oxidized forms NAD^+ and $NADP^+$ [6]. Pyridinedicarboxylic acids and their derivatives belong to an interesting series of compounds with biological applications. Vanadium complexes of pyridinedicarboxylic acids are interesting molecular model systems because they are potential agents for treating insulin-dependent diabetes mellitus [7].

1,10-Phenanthroline and its derivatives are biologically important chelating ligands. A consequence of the planar nature of 1,10-phenanthroline is its ability to participate as a DNA intercalator [8]. Some metal complexes containing 1,10-phenanthroline are also known to bind to DNA by an intercalative mode [9–11]. Several metal complexes with 1,10-phenanthroline and natural products incorporating this heterocyclic nucleus process interesting anticancer properties [12–14]. 1,10-Phenanthroline and its congener bipyridyl form complexes with vanadium in 0, +3, +4 and +5 oxidation states [15–18]. The vanadium(III) cationic complex $[V_2(\mu\text{-}O)(phen)_4Cl_2]Cl_2$ prepared by the action of VCl_3 on 1,10-phenanthroline was shown to interact with DNA leading to its degradation [19,20]. Synthesis of mononomeric V(III) complexes has long been a challenge in V(III) coordination chemistry. Reaction of ammonium vanadium sulphate and vanadium(III) sulphate with 1,10-phenanthroline gave purple complexes containing vanadium (IV) [21].

In the present article, the electrochemical and spectral properties of binary and mixed-ligand oxovanadium(IV) complexes involving diimines and dipicolinic acid formed in dimethylsulfoxide (DMSO) are reported. The structures of DPA and diimine ligands are given below.

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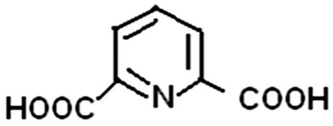
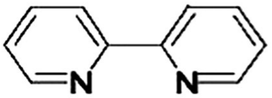
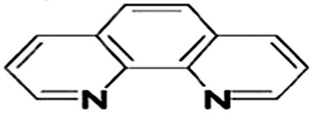


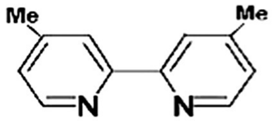
dipicolinic acid (DPA)



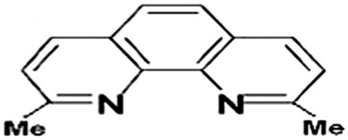
2,2'- bipyridine
(bipy)



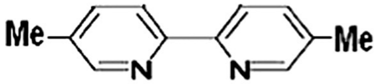
1,10-phenanthroline
(phen)



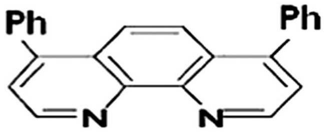
4,4'-dimethyl-2,2'- bipyridine
(4,4'-Me$_2$ bipy)



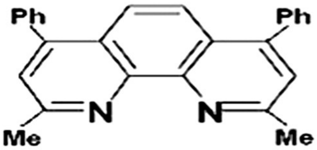
2,9-dimethyl-1,10-phenanthroline
(dmp)



5,5'-dimethyl -2,2'- bipyridine
(5,5'-Me$_2$ bipy)



4,7-diphenyl -1,10-phenanthroline
(bathophen)



4,7-diphenyl –2,9-dimethyl-1,10-phenanthroline
(bathocuproin)

2. Experimental

All the chemicals used in the present investigation were procured from commercial sources and were used as such. 4 mM solution of VOSO$_4$ in dimethyl sulfoxide (DMSO) was used in both the binary and mixed-ligand complexes of oxovanadium(IV). All the cyclic voltammograms were recorded in DMSO containing 0.2 M of NaClO$_4$ as a supporting electrolyte.

The software driven BAS Electrochemical Systems, Model EPSILON (Bioanalytical Systems, Inc, USA) was employed for all the electrochemical studies. The working electrode was glassy carbon disc electrode (GCE), the counter electrode was a platinum wire and reference electrode Ag/AgCl in saturated KCl ($E^0 = +199$ mV vs. NHE). Purging and blanketing of nitrogen (99.999% pure) were done for analytic solution placed in the electrochemical cell of 15 ml capacity for 30 min. Great care was taken in the electrode pretreatment. Mechanical polishing of the working electrode (GCE) was done over a velvet microcloth with an alumina suspension. All the electrochemical experiments were performed at a constant temperature of 25 ± 0.5 °C. IR compensation and background subtraction have been also done. Electronic absorption spectra of the complexes have been recorded in DMSO at room temperature by Perkin-Elmer UV–Visible Spectrophotometer Model Lambda-35.

3. Results and discussion

3.1. Cyclic voltammetric properties of binary oxovanadium(IV)-diimine complexes A, B, C, D and E

Five types of binary oxovanadium(IV) diimine complex species **A**, **B**, **C**, **D** and **E** formed in 1:2 VOSO$_4$:diimine molar ratio in dimethyl sulfoxide. The complex species named as $[VO(4,4'\text{-}Me_2bipy)_2]^{2+}$ (**A**), $[VO(5,5'\text{-}Me_2bipy)_2]^{2+}$ (**B**), $[VO(dmp)_2]^{2+}$ (**C**), $[VO(bathophen)_2]^{2+}$ (**D**) and $[VO(bathocuproin)_2]^{2+}$ (**E**). Electron transfer properties (redox reaction) of all five complexes were studied in DMSO. It cannot be possible to come any proton from pure DMSO solvent in the redox process. Various researchers have investigated the electron transfer properties of vanadium complexes in dimethylsulfoxide with the help of cyclic voltammetry [22,23]. It has earlier been reported that 2,2′-bipyridyl, 1,10-phenanthroline and their derivative show reversible couple at a very high negative potential (≥−1.9 V vs. SCE) corresponding to L^0/L^- change both in aqueous and non-aqueous media [24]. The electrochemical measurement results of these five complex solutions in scan rate range of 25–200 mVs^{-1} are given in Table 1.

The cyclic voltammograms of binary complexes **A** and **B** were almost similar except that the first irreversible reduction peak at $Epc_1 = -1042$ mV was well-defined in the former case (Table 1)