

Redox Behaviour of a Tris(pyrazolyl)methanesulfonate Vanadium Complex, a Preliminary Study

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Abstract

The electrochemical behaviour of the new vanadium(IV) complex [VCl₃(SO₃Cpz₃)] (pz = pyrazolyl), obtained by reaction of VCl₃ with Li[SO₃Cpz₃], investigated by cyclic voltammetry and controlled potential electrolysis is reported and compared with those of hydrotris(pyrazolyl)borate vanadium(IV) complexes.

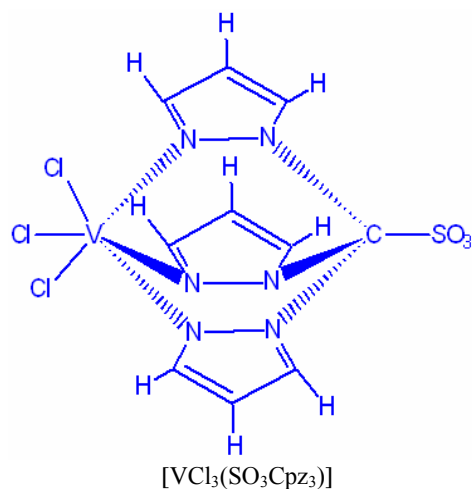
Keywords: Vanadium complexes, Tris(1-pyrazolyl)methanesulfonate; Tripodal ligands; Cyclic voltammetry.

Introduction

Tris(1-pyrazolyl)methanesulfonates, SO₃Cpz₃⁻ (pz = pyrazolyl), with three N-deprotonated pyrazole rings bound to a carbon atom, hydrolytically stable and soluble in polar protic solvents, constitute a rather promising class of tripodal N-donor ligands in modern coordination chemistry [1]. However, vanadium complexes containing these ligands have not been reported so far.

We have been able [2] to synthesise the first tris(1-pyrazolyl)methanesulfonate vanadium(IV) complex, [VCl₃(SO₃Cpz₃)] (pz = pyrazolyl), derived from vanadium(III) chloride in the presence of lithium tris(1-pyrazolyl)methanesulfonate, which was completely characterized by IR and EPR spectroscopy, FAB-MS spectrometry and elemental analysis. Its electrochemical behaviour is described as follows.

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Results and discussion

The redox properties of the vanadium complex [VCl₃(SO₃Cpz₃)] (pz = pyrazolyl) were studied by cyclic voltammetry (CV) in a two-compartment three-electrode cell, at a Pt disc working electrode ($\phi = 500 \mu\text{m}$) and by controlled potential electrolysis (CPE), in a three-compartment three-electrode cell, at a Pt gauze working electrode, by using an EG&G PAR 273A potentiostat/galvanostat. Both techniques were carried out in an inert atmosphere (N₂), at room temperature, in a non-aqueous aprotic medium, 0.2 M [Bu₄N][BF₄]/CH₂Cl₂. The redox potentials are quoted relative to the SCE by using as internal reference the ferrocene/ferricinium couple ($E_{1/2}^{\text{ox}} = 0.525 \text{ V vs. SCE in CH}_2\text{Cl}_2$).

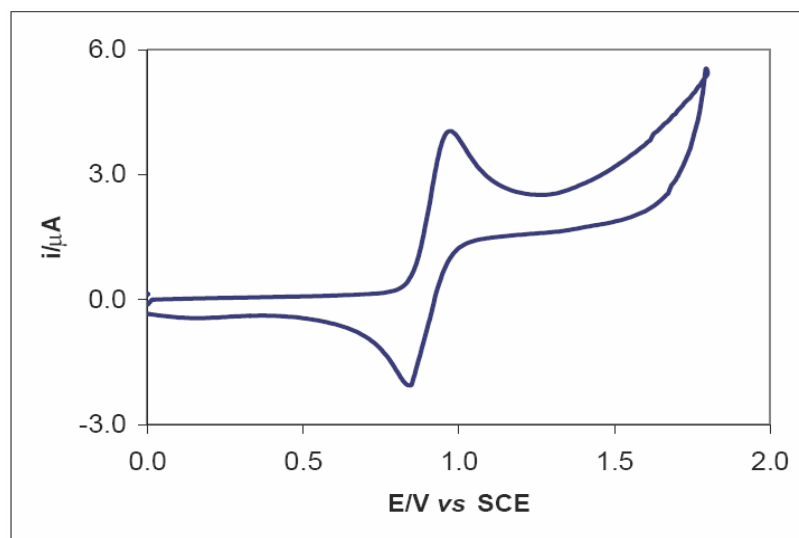


Figure 1. Cyclic voltammogram of the complex [VCl₃(SO₃Cpz₃)] at a Pt disc electrode, in a 0.2 M [Bu₄N][BF₄]/CH₂Cl₂ solution ($\nu = 0.2 \text{ Vs}^{-1}$).

This complex exhibits only one single-electron (CPE) fully reversible ($i_{pa}/i_{pc}=1$; $\Delta E \cong 70$ mV) oxidation wave at $E_{1/2}^{ox} = 1.14$ V vs. SCE corresponding to the oxidation of V(IV) to V(V) (Fig. 1), whereas lithium tris(1-pyrazolyl)methanesulfonate is electrochemically inert in the potential range from -2.0 V to $+2.0$ V, at the above experimental conditions.

The V^{IV/V} redox potential of our complex lies within the range of those reported for other V^{IV} complexes with related tripodal ligands, namely the hydrotris(1-pyrazolyl)borate oxovanadium(IV) complexes [3] indicated in Table 1, which also undergoes a single-electron oxidation, although not fully reversible at the studied cyclic voltammetric time scale.

Table 1. Oxidation potential of vanadium(IV) complexes in CH₂Cl₂.

Complex	E° (V vs. SCE)
[VCl ₃ (SO ₃ CpZ ₃)]	1.14
[VO(HBpz ₃)(acac)]	1.21
[VO{HB(3,5-Me ₂ pz) ₃ }(acac)]	1.07
[VO(Cl)(HBpz ₃)(DMF)]	1.33
[VO(Cl){HB(3,5-Me ₂ pz) ₃ }(DMF)]	1.21

(acac = acetilacetone; DMF = dimethylformamide)

Final comments

We are now extending the synthetic and electrochemical study to derivatives of [VCl₃(SO₃CpZ₃)] and to other metal tris(pyrazolyl)methanesulfonate complexes in order to attempt establishing redox potential-structure and -composition relationships.

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