STUDY OF THE REDOX PROPERTIES OF TETRAKIS(PYRAZOLYL)BORATE RHENIUM(V) COMPLEXES

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Summary

The redox properties of some tetrakis(pyrazolyl)borate rhenium(V) complexes of the types $[ReO\{\eta^3\text{-}B(pz)_4\}L]$($L= {}^-O^\frown O^-$ type ligand, $1/2L= MeO^-$) and $[ReO\{\eta^2\text{-}B(pz)_4\}(OMe)L']$ ($L'= O^\frown O^-$, $N^\frown O^-$, $N^\frown N^-$ type ligands) were studied by cyclic voltammetry. These Re(V) complexes display generally one anodic and one cathodic waves, at values of potential which are discussed in terms of the hapticity of the pyrazolylborate ligand and of the electronic properties of the chelating co-ligands.

Introduction

Tetrakis(pyrazolyl)borate ($B(pz)_4^-$) is a versatile ligand, in particular from a coordination point of view, which stabilizes either high or low oxidation states of rhenium [1,2,3].

Although ($B(pz)_4^-$) acts usually as a tridentate ligand there are examples where it acts as a bidentate or bis-bidentate ligand [4].

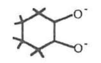
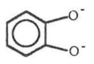
The conversion of the tridentate tetrakis(pyrazolyl)borate on $[ReO\{\eta^3\text{-}B(pz)_4\}(OMe)_2]$ to the η^2-coordinated mode in $[ReO\{\eta^2\text{-}B(pz)_4\}(OMe)L']$ was observed [3] to be induced in reactions with chelating monoanionic ligands.

In order to have a better insight into the electronic properties of η^3- and η^2-$B(pz)_4$ rhenium(V) centres, and on the influence of mono- or di-anionic chelating co-ligands on the electrochemical behaviour of complexes of the types [ReO{η^3-B(pz)$_4$}L](L= $^{-}O^\frown O^{-}$ type ligand, 1/2L= MeO$^-$) and [ReO{η^2-B(pz)$_4$}(OMe)L′] (L′= $O^\frown O^{-}$, $N^\frown O^{-}$, $N^\frown N^{-}$ type ligands) their redox properties were studied and are now reported.

Results and discussion

The electrochemical behaviour of the complexes, studied by cyclic voltammetry and in a few cases also by controlled potential electrolysis, at platinum wire or platinum gauze electrodes, in 0.2 M [NBu$_4$][BF$_4$] / CH$_3$CN solutions, show that the [ReO{η^3-B(pz)$_4$}L] complexes display one partially reversible anodic wave and one irreversible cathodic wave, although compound (**8**) displays one irreversible oxidation wave and a partially reversible reduction process, whereas no cathodic process was detected for complex (**1**) within the range of potentials available (Table 1). The potentials are quoted *versus* S.C.E. and were measured at 200 mVs^{-1} using ferrocene ($E_{1/2}^{ox}$=0.40 V) as internal standard.

Table 1 -Cyclic voltammetric data$^{(a)}$ for complexes [ReO{η^3-B(pz)$_4$}L]

L		$E_{1/2}^{ox}$	E_p^{red}
OMe$^-$ (1/2 L)	(**1**)	0.78	—
OCH$_2$CH$_2$O^{2-}	(**2**)	1.08	-1.98
OCH(CH$_3$)CH$_2$O^{2-}	(**3**)	1.05	-1.78
OCH(CH$_3$)CH(CH$_3$)O^{2-}	(**4**)	1.01	-1.88
OC(CH$_3$)$_2$C(CH$_3$)$_2$O^{2-}	(**5**)	1.02$^{(b)}$	-1.84
OCH$_2$CH$_2$CH$_2$O^{2-}	(**6**)	0.82	-1.72
	(**7**)	0.96	-1.78
	(**8**)	1.22$^{(b)}$	-1.29$^{(c)}$

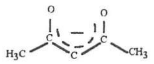
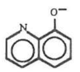
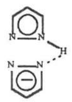
$^{(a)}$ Values in Volt (± 20 mV) *vs*. S.C.E., measured at 200 mV/s in 0.2 M [NBu$_4$][BF$_4$] / CH$_3$CN, using [Fe(η^5-C$_5$H$_5$)$_2$] ($E_{1/2}^{ox}$=0.40 V) as internal standard. $^{(b)}$ Irreversible wave, E_p^{ox}. $^{(c)}$ Reversible wave ($E_{1/2}^{red}$).

The range of potential values measured for complexes (**1-8**) points to a significant influence of the characteristics of the dianionic oxygen donor ligands on the redox properties of the complexes. The lowest oxidation potential value was measured for the dimethoxy compound (**1**), suggesting that the two methoxide ligands present a stronger electron donor ability than the O-chelating ligands. This is also consistent with the fact that no reduction process is detected for complex (**1**) within the acessible potential range, in view of the values (close to the low potential limit) measured for complexes (**2-7**).

Complexes (**2-5**) display similar oxidation potential values, the replacement of H by CH$_3$ corresponding to a small decrease on the value of the potential, as expected, as a consequence of the slightly better electron donor properties of the CH$_3$ group compared to H.

The possible influence of stereochemical effects is recognized by the lower oxidation potentials of (**7**) compared with (**2**), and of (**6**) (with a six membered chelating ring) compared with (**2-5**) (with a five membered ring).

Table 2- Cyclic voltammetric data$^{(a)}$ for complexes [ReO{η^2-B(pz)$_4$}(OMe)L′]

L′		E_p^{ox}	$E_{1/2}^{red}$
	(**9**)	1.56$^{(b)}$	-1.38
	(**10**)	1.30	-1.21
	(**11**)	1.30	-1.08

$^{(a)}$ Values in Volt (± 20 mV) *vs*. S.C.E., measured at 200 mV/s in 0.2 M [NBu$_4$][BF$_4$] / CH$_3$CN, using [Fe(η^5-C$_5$H$_5$)$_2$] ($E_{1/2}^{ox}$=0.40 V) as internal standard. $^{(b)}$ Displays some reversibility.

The higher oxidation and reduction potentials observed for complex (**8**), compared to the related complexes (Table1) point to a lower electron density at the metal centre in the former case, possibly as a consequence of an extended electronic delocalization along the aromatic π-system, the aromatic diolate acting as an efficient electron withdrawing ligand.

Each of the complexes $[ReO\{\eta^2\text{-}B(pz)_4\}(OMe)L']$ **(9-11)** with the dihapto $(B(pz)_4^-)$ ligand displays, by cyclic voltammetry, an irreversible oxidation and a partially reversible reduction wave at the values of potential indicated in table 2.

Although a smaller number of η^2-$B(pz)_4$ complexes have been studied, one observes that they exhibit higher oxidation potentials than those of the η^3-$B(pz)_4$ compounds, possibly suggesting that the η^2-$B(pz)_4$ pyrazolylborate has a stronger stabilizing effect on the HOMO than the η^3-ligand.

Controlled potential electrolysis performed at the potential of the anodic and the cathodic waves of the complex **(2)** allowed the determination of one and two electrons per molecule, respectively. Furthermore, chemical reactivity is induced by anodic electrolysis, in spite of the reversible character of the anodic wave observed in the time scale of cyclic voltammetry. The characterization of the products is under way.

Acknowledgements

This work was partially supported by Junta Nacional de Investigação Científica e Tecnológica (JNICT).

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STUDY OF THE REDOX PROPERTIES OF IRON (III), COPPER (II) AND PALLADIUM (II) CAMPHOR COMPLEXES

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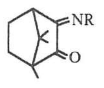
Summary

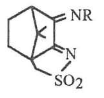
The redox properties of complexes of general formulæ $[\{FeCl_3L\}_2]$, $[\{CuCl_2L\}_2]$ and $[PdCl_2L_2]$ (L=camphor-type ligand) were studied by cyclic voltammetry and controlled potential electrolysis. As a general behaviour, the complexes display at least one cathodic wave which has a marked metal character. The potentials are discussed on the basis of the electronic properties of the camphor-type ligands. Extensive reductive controlled potential electrolysis of one of the diiron complexes allowed the electrosynthesis of a mononuclear product. The electrochemical behaviour of the L ligands [L=A (R=Ph or Pr^i) and L=B ($R=NH_2$)] is also reported.

Introduction

Within our interest on the coordination chemistry of camphorimine ligands we have prepared some palladium complexes with such ligands [1]. Their electrochemical behaviour, studied by cyclic voltammetry, showed that there is a marked effect of the characteristics of the camphorimine ligand on the redox potential of the metal site, *i.e.* the ketone-type ligands (A) strongly influence the redox potentials in contrast with a slight effect observed for the sulfonimide-type ligands (B). In order to further investigate that effect we now extend the study to other camphor type (A) or (B) ligands. Moreover, camphorimine iron(III) and copper(II) complexes were prepared and the study of their redox properties show that a metal centred reduction process takes place.



(A)



(B)

Portugaliæ Electrochimica Acta, 13 (1995) 309-313