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Cu (II) and Hg(II) captopril compounds in aqueous media: A calorimetric study

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Abstract The interactions in aqueous solution of captopril with Cu(II) and Hg(II) cations are investigated through solution calorimetry. The reactions and respective enthalpy values (kJ mol^{-1}) are: Cu^{2+} (aq) + Captopril (aq) → [Cu.Captopril]$^{2+}$ (aq), -27,25; Cu^{2+} (aq) + 2 Captopril (aq) → [Cu.2 Captopril]$^{2+}$ (aq), -28,37 and Hg^{2+} (aq) + Captopril (aq) → [Hg.Captopril (aq)]$^{2+}$ (aq), -90,34. The soft acid-soft base: Hg(II)-S interaction it is pointed out as the main responsible for the higher captopril-Hg(II) interaction, in comparison with the captopril-Cu(II).

Keywords Captopril; Solution Calorimetry; Copper; Mercury.

Introduction

Captopril (CAS nº 62571-86-2), (2S)-1-[(2S)-2-methyl-3-sulfanylpropanoyl]pyrrolidine-2-carboxylic acid, (Fig. 1) , it is anorally active antihypertensive agent having a uniqueinhibitory action on the angiotensin-converting enzyme (ACE) of the renin-angiotensin system [1]. It is widely utilized in the treatment of hypertension, congestive heart failure and heart attack in both mono and combination therapy.

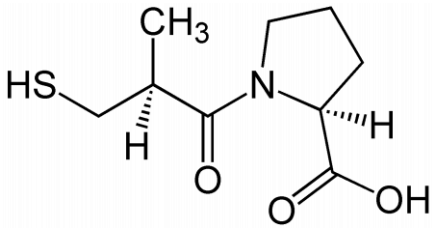

Figure 1: Structural formula of Captopril

The interaction (trough complex formation) of captopril with transition metals have been investigated [2], such as in the electrochemical cadmium determination based on the formation of a cadmium-captopril complex [3], or the kinetic study, based on TG data, of the thermal degradation of Cu(II), Ni(II), Sn(II) and Fe(III) captopril complexes [4].

However, there is a lack of calorimetric studies focusing on the captopril interactions with transition metals. Since captopril it is an oral drug, interactions in aqueous media are particularly relevant. In this connection, in the present work the captopril interactions with Cu(II) and Hg(II) in aqueous solutions are investigated by solution calorimetry.

Experimental

The study ofCu(II) and Hg(II) captopril interactions were performed in aqueous (deionized) solution, employing copper sulphate and mercury nitrate as metal cations sources. The interactions were investigated by solution calorimetry (ampoule break procedure) in a LKB2277 calorimeter.

Results and Discussion

The obtained solution calorimetry results are summarized in Tables 1-3. As can be verified, the dissolution of captopril in the metal cations solutions is exothermic, whereas the dissolution of captopril in water is endothermic. So, can be concluded that there are, indeed, a strong interaction between captopril molecules and the metal cations in the presence of water molecules.

Table 1: Dissolution enthalpy results to the dissolution in water and aqueous solutions of Cu(II) and Hg(II).

Compound	Solvent	Dissolved mass/mg	ΔH/kJmol^{-1}
Captopril (s)	water	26,0	11,78
		24,3	12,71
		28,0	12,48
		36,0	12,86
		19,2	11,66
	Cu^{2+}(aq) (1:1)	27,0	-14,81
		32,0	-14,40
		18,3	-16,27
		26,1	-15,10
		24,0	-14,85
	Cu^{2+}(aq) (1:2)	26,4	-17,42
		23,0	-16,67
		22,0	-16,23
		25,0	-15,82
		34,0	-15,66
		30,0	-15,20
		29,8	-15,77
	Hg^{2+} (aq) (1:1)	31,0	-78,37
		30,0	-81,07
		31,0	-76,64
		19,7	-76,22

Table 2: Dissolution enthalpy for captopril in water and aqueous solutions of Cu(II) and Hg(II) (average values).

Compound	Solvent	ΔH/kJmol^{-1}
Captopril (s)	water	12,26 ± 0,4
	Cu^{2+} (aq) (1:1)	-15,09 ± 0,5
	Cu^{2+} (aq) (1:2)	-16,11 ± 0,8
	Hg^{2+}(aq) (1:1)	-78,08 ± 8,9

Table 3: Enthalpies of the Cu(II) and Hg(II) captopril complex formation in aqueous solution.

Reaction	ΔH/kJmol^{-1}
Cu^{2+} (aq) + Captopril (aq) → [Cu.Captopril]$^{2+}$ (aq)	-27,25
Cu^{2+} (aq) + 2 Captopril (aq) → [Cu.2 Captopril]$^{2+}$ (aq)	-28,37
Hg^{2+} (aq) + Captopril (aq) → [Hg.Captopril (aq)]$^{2+}$ (aq)	-90,34

Furthermore, the dissolution of captopril in a 1:1 (mo:mol) or 1:2 Cu(II) solution are identical (in the uncertainty interval). So, can be concluded that an increase of the total amount of captopril in solution do not provoke "extra" captopril-copper interactions, probably due to the fact that all available coordination sites of Cu^{2+} are already interacting.

The most remarkable result is related with the captopril-Hg(II) interaction, which it is 3.3 times most exothermic than the captopril-Cu(II) interactions. Such fact can be explained that Hg(II) is a soft acid, whereas Cu(II) is a hard (or borderline) one. The captopril-Hg(II) is supposed to occur, essentially, through S^{-2} which it is a soft base. As previously verified by FTIR and Raman spectra to diorganotin(IV) complexes of captopril [5], the coordination of Cap can involve a C=O group and a S atom of the SH deprotonated group. Indeed, employing Pt(IV) complexes as oxidant agents, it was verified that thefullydeprotonated captopril is about $10^5$to 10^6times more reactive than its corresponding thiol form [6].

On the other hand, the captopril-Cu(II) interactions occurs, essentially, through a Lewis acid-Lewis base bons involving the N and O atoms. It was previously verified [2] that in aqueous solution at a molar ratio of Cu:Cap 1:2 and ambient temperature, copper(II) is reduced to copper(I) which forms with an excess of captopril a yellow diamagnetic Cu(I) complex.

To the solid state $Cu_2(Cap)_2(H_2O)$ complex it was verified that there are the participation of COOH, C=O and SH groups in coordination, together with H_2O, which is also included in the inner coordination sphere of copper [2]. In the present work, it is assumed, to the aqueous solution captopril-Cu(II) interactions, a similar coordination feature.

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