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**SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL BEHAVIOUR OF
MIXED LIGAND COMPLEXES OF COBALT (III)
WITH DIMETHYLGLYOXIME AS THE PRIMARY LIGAND AND
TYROSINE, VALINE OR THREONINE AS THE SECONDARY ONE**

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ملخص:

تم اصطناع معقدات كوبالوكسيم جديدة ذات الصيغة $[Co(Hdmg)_2 (Tyr) X] nH_2O$ = شرحية أحادية لثنائي ميثيل جلوكسيم، Tyr = تيروسين و I, Br, Cl = X أو SCN وكذا الصيغة $[Co(Hdmg)_2(HA)NO_2].nH_2O$ = تريونين HA، [Co(Hdmg)₂(HA)NO₂].nH₂O و فالين (Val). عينت خواص كل هذه المعقدات بطرق تحليل أولي: قياس الناقلية، IR، RMN، و معطيات طيف إلكتروني. بينت نتائج الناقلية الجزيئية أن هذه المعقدات غير كهروليتيّة، كما أن لأطيافها الإلكترونية ثلاث عصب مشابهة كما في كوبالوكسيمات. أفادت الدراسات الكهروكيميائية أن معقدات الكوبالت تخضع إلى مرحلتين إرجاع أحادي إلكترونية وفق.

ABSTRACT

Two new series of cobaloxime complexes of formulae $[Co(Hdmg)_2 (Tyr) X] nH_2O$, (Hdmg = the monoanion of dimethylglyoxime, Tyr = thyrosine and X = Cl, Br, I or SCN) and $[Co(Hdmg)_2(HA)NO_2].nH_2O$, [HA = threonine (Thr) and valine (Val)] have been synthesized. All the complexes are characterized by elemental analyses, conductivity measurements, IR, ¹H NMR and electronic spectral data. The molar conductivity data show them to be non-electrolytes. The electronic spectra of these compounds show three bands, similar to those generally found for cobaloximes. Electrochemical studies suggest that the cobalt complex undergoes two single one electron reduction steps corresponding to $Co(III) \rightarrow Co(II)$ and $Co(II) \rightarrow Co(I)$.

RESUME

Deux nouvelles séries de cobaloximes de formule générale $[Co(Hdmg)_2 (Tyr) X] nH_2O$, (Hdmg = monoanion de la diméthylglyoxime, Tyr = thyrosine et X = Cl, Br, I or SCN) et $[Co(Hdmg)_2(HA)NO_2].nH_2O$, [HA = thréonine (Thr) et valine (Val)] ont été préparées. Tous les complexes ont été caractérisés par analyse élémentaire, conductimétrie et par spectrométrie IR, RMN du proton et électronique d'absorption. Les mesures de conductivité molaire indiquent qu'il s'agit de non électrolytes, alors que les spectres électroniques d'absorption comportent trois bandes et sont similaires à ceux des autres cobaloximes. Les données électrochimiques suggèrent que les complexes subissent deux réductions successives correspondant à $Co(III) \rightarrow Co(II)$ and $Co(II) \rightarrow Co(I)$.

INTRODUCTION

The bis-(dimethylglyoximato) cobalt(III) system, generally referred to as a cobaloxime, has been subject of intense study as a model for vitamin B₁₂ chemistry [1].

We have previously reported the synthesis and studies of cobaloxime complexes of the type $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{X}]n\text{H}_2\text{O}$ (When HA = Glycine, serine, cysteine and cystine). These compounds were structurally characterized [2,3]. We now report on the synthesis and properties of two new series of cobaloxime complexes of general formulae $[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{X}]n\text{H}_2\text{O}$ (Hdmg = monoanion of dimethylglyoxime, Tyr = tyrosine and X = Cl, Br, I or SCN) and $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{NO}_2].n\text{H}_2\text{O}$, HA = valine (val) or threonine (Thr).

The number of electrochemical studies of these compounds has also increased [4,5]. The experienced possibility of easy transition between the different oxidation states of the metal atom, predict rich redox properties to these complexes. Moreover, oxido-reductive conversion between the three oxidation states [Co(III), Co(II) and Co(I)] should play a fundamental role in the chemistry of cobaloximes [6].

EXPERIMENTAL

Materials

All chemical reagents and solvent used in the synthesis of complexes were Fluka p.a. grade products and used without further purification.

The amino acids used are tyrosine: L(-)-Tyr, valine: L(+)-Val and threonine: L(-)-Thr and were p.a. grade.

Preparation of complexes

Complex $[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{Cl}].2\text{H}_2\text{O}$.

To a solution of $\text{CoCl}_2.6\text{H}_2\text{O}$ (2.37g, 10 mmol) in ethanol (55 mL) were added solid H₂dmg (2.32g, 20 mmol) and amino acid (Tyr) (1.84g, 10 mmol). Air oxidation was achieved with constant stirring.

Stirring was continued for 3 h at room temperature. The reaction mixture was then allowed to settle. The precipitated solid brown-green was collected by filtration, washed with ethanol, followed by diethyl ether and dried in air.

Complexes $[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{X}].n\text{H}_2\text{O}$ (X = Br, I or SCN).

To a solution of $\text{Co}(\text{NO}_3)_2.6\text{H}_2\text{O}$ (2.91g, 10 mmol) in ethanol (65 mL) were added solids H₂dmg (2.32g, 20 mmol), amino acid (Tyr) (1.84g, 10 mmol) following after 5 min by NaBr (1.02g, 10 mmol), NaI (1.49g, 10 mmol) or KSCN (0.98g, 10 mmol).

The mixture was subsequently stirred and air oxidation was achieved for a further 3 h 30 min (for the bromo and iodo complexes) and 5 h 30 min (for a thiocyanato complex). During which times brown solids precipitated, which were isolated by filtration and washed with ethanol and diethyl ether. The solids were dried in air.

Complexes $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{NO}_2].n\text{H}_2\text{O}$ (HA = Val or Thr).

The complexes were prepared by the method described above, using the same molar quantities reagents.

Physical measurements

Microanalyses were performed at the service d'analyse du CNRS (Vernaison-France). Conductance values were obtained with a Tacussel CD-810 conductimeter at room temperature from 10^{-3} mol L⁻¹ solutions of complexes in DMSO. IR spectra were recorded with KBr pellets in the range 400-4000cm⁻¹ on a Shimadzu FTIR-9101 M spectrophotometer.

The electronic absorption spectra of complexes in DMSO solutions (5.10^{-3} mol.L $^{-1}$ for visible and 5.10^{-5} mol.L $^{-1}$ for UV) were measured on a Shimadzu UV-1601 UV-Visible spectrophotometer in the range 250-950 nm.

The ^1H NMR were recorded on a Jeol Gsx 270 MSB (270 MHz) spectrophotometer in DMSO- d_6 solution for the complexes and for the dimethylglyoxime ligand and in D_2O solution for the aminoacid ligands using TMS as internal reference (service commun de RMN, université d'Angers).

Electrochemical measurements were performed with a 273 EGG potentiostat- galvanostat.

Cyclic voltammograms were obtained by using a glassy carbon disc RDE (250 rpm) as working electrode, a platinum wire as auxiliary and a silver wire immersed in electrolyte solution as pseudo reference electrode. Both the reference electrode and the counter electrode were separated from the analyte solution by a fritted glass bridge.

Electrochemical measurements were made under a dinitrogen atmosphere, all electrochemical data were collected at 25°C.

RESULTS AND DISCUSSION

The cobalt(III) complexes of bis-(dimethylglyoximato) with amino acids Tyr, Val and Thr have been prepared. The chemical analyses data of these complexes are given in table 1. The molar conductance of cobalt(III) complexes in DMSO are in the range 4-35 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

IR Spectra

Important IR spectral bands of amino acids, dimethylglyoxime and their complexes are given in table 2.

No absorption in the usual NH Stretching region 3500-3300 cm^{-1} is shown by the amino acids. Instead a weak band appears in the 3090-3030 cm^{-1} region for Val and Thr, and at 3190 cm^{-1} for Tyr due to the NH_3^+ group. This band is assigned to the NH_3^+ stretching mode [7]. In the complexes of a Tyr, the absorption corresponding to the stretching mode of the NH_2 group is located at 3230 - 3205 cm^{-1} region and in $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{NO}_2]$ (HA = Val or Thr) at 3230 cm^{-1} .

The IR spectra of Val and Thr show a weak band at 1618 cm^{-1} characteristic of $\delta(\text{NH}_3^+)$ [7,8]. Upon coordination to a metal, it is shifted to higher frequency. Thus in $[\text{Co}(\text{Hdmg})_2(\text{Val})\text{NO}_2]$ this band is found at 1625 cm^{-1} and in $[\text{Co}(\text{Hdmg})_2(\text{Thr})\text{NO}_2]$ at 1635 cm^{-1} . In the complexes of Tyr, $\delta(\text{NH}_2)$ occurs at around 1610 cm^{-1} region.

The infrared spectrum of the amino acids shows two absorptions corresponding to the asymmetric and symmetric modes. $\nu_{\text{as}}(\text{COO}^-)$ appears in the 1625-1575 cm^{-1} range and $\nu_{\text{s}}(\text{COO}^-)$ in the 1425-1364 cm^{-1} range. These can be assigned to the ionic carboxyl absorption [8, 9]. In the complexes of Tyr, the $\nu_{\text{as}}(\text{COO}^-)$ is observed at 1589-1560 cm^{-1} region, and $\nu_{\text{s}}(\text{COO}^-)$ at 1385-1364 cm^{-1} region. While in $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{NO}_2]$ (HA = Val, Thr) $\nu_{\text{as}}(\text{COO}^-)$ appears at 1574 and 1570 cm^{-1} , respectively for the complexes with Val and Thr. $\nu_{\text{s}}(\text{COO}^-)$ is located at 1385 cm^{-1} for $[\text{Co}(\text{Hdmg})_2(\text{Thr})\text{NO}_2]$ and at 1366 cm^{-1} for $[\text{Co}(\text{Hdmg})_2(\text{Val})\text{NO}_2]$, this suggest the coordination of aminoacids to metal [10].

In the infrared spectra of H_2dmg , the sharp band of medium intensity occurring at 1447 cm^{-1} is attributed to $\nu(\text{C}=\text{N})$ of the oxime. This band is shifted to lower frequency at approximately 1418 cm^{-1} in the $[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{X}]\cdot n\text{H}_2\text{O}$ complexes, an to higher frequency at 1452 cm^{-1} in the complexes of Val and Thr [11, 12] showing coordination with metal occur.

In all the complexes, the strong as well as sharp band between 1144 and 1155 cm^{-1} is due to the N-O stretching vibration [11, 12].

The metal sensitive as well as sharp band at 750-740 cm^{-1} region may be attributed to C=N-O deformation vibration [12].

Table 1: Analytical data of the complexes

Compound formula	F.Wt	Color	Yield (%)	Anal. Found (calc.) (%)					
				C	H	N	Co	X ^b	
[Co(Hdmg) ₂ (Tyr)Cl].2H ₂ O	541.38	Brown-green	40	38.1 (37.7)	5.1 (5.3)	12.7 (12.9)	10.3 (10.8)	6.8 (6.5)	
Co C ₁₇ H ₂₉ N ₅ O ₉ Cl									
[Co (Hdmg) ₂ (Tyr)Br].2H ₂ O	585.83	Brown-Light	35	34.4 (34.8)	4.7 (4.9)	12.1 (11.9)	10.3 (10.0)	13.9 (13.6)	
Co C ₁₇ H ₂₉ N ₅ O ₉ Br									
[Co (Hdmg) ₂ (Tyr)I]	596.93	Brown-Rousse	50	33.8 (34.1)	3.9 (4.1)	11.8 (11.7)	9.9 (9.8)	20.9 (21.2)	
Co C ₁₇ H ₂₅ N ₅ O ₇ I									
[Co (Hdmg) ₂ (Tyr)SCN]	527.93	Brown-Light	60	40.6 (40.9)	4.6 (4.7)	15.9 (15.9)	11.3 (11.1)	6.4 (6.0)	
Co C ₁₈ H ₂₃ N ₆ O ₇ S									
[Co (Hdmg) ₂ (Val)NO ₂]	452.28	Brown-Light	40	34.1 (34.4)	5.3 (5.5)	18.6 (18.5)	13.2 (13.0)	-	
Co C ₁₃ H ₂₃ N ₆ O ₈									
[Co (Hdmg) ₂ (Thr)NO ₂]	454.25	Brown-Rousse	35	31.4 (31.7)	4.9 (5.0)	18.8 (18.6)	12.8 (12.9)	-	
Co C ₁₂ H ₂₃ N ₆ O ₉									

^bX= Cl, Br, I, or SCN

Table 2: Important IR bands and their assignments

Compound	ν (NH_3^+)	δ (NH_3^+)	ν_{as} (COO^-)	ν_{sy} (COO^-)	ν ($\text{C}=\text{N}$)	ν (NO)	δ (NO)	ν (Co-N)	ν (NCS)
Tyr	3190 w	1611 w	1583 w	1364 w	-	-	-	-	-
Val	3090 w	1618 w	1575 b	1425 w	-	-	-	-	-
Thr	3030 w	1618 w	1625 s	1414 w	-	-	-	-	-
$[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{Cl}]2\text{H}_2\text{O}$	3205 w	1608 w	1589 w	1365 s	1418 w	1155 w	739 s	507 s	-
$[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{Br}]2\text{H}_2\text{O}$	3206 w	1612 w	1583 b	1366 s	1418 s	1153 w	741 s	509 s	-
$[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{I}]$	3210 w	1609 w	1570 w	1385 s	1417 w	1153 w	741 w	511 s	-
$[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{SCN}]$	3190 w	1609 w	1560 w	1364 w	1415 w	1151 w	741 b	515 s	2178 s
$[\text{Co}(\text{Hdmg})_2(\text{Val})\text{NO}_2]$	3230 w	1625 w	1574 w	1366 b	1452 s	1144 w	756 b	509 s	-
$[\text{Co}(\text{Hdmg})_2(\text{Thr})\text{NO}_2]$	3230 w	1635 w	1570 b	1385 s	1452 w	1144 w	744 b	509 s	-

Abbreviations: s = strong, w = weak, b = broad

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An unique feature in the occurrence of a new strong and sharp band at a 509 cm^{-1} in the $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{NO}_2] \cdot n\text{H}_2\text{O}$ complexes, and in the $509\text{--}515\text{ cm}^{-1}$ range in the complexes of Tyr that are not found in the ligands. In detailed infrared studies on cobaloximes by Yamazaki and Hohokabe [13], the former band is assigned to the $\nu(\text{Co-N})$ vibrations. $[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{SCN}]$ exhibits a very strong and sharp band at 2178 cm^{-1} assignable to $\nu(\text{NCS})$ of the coordinated thiocyanate.

The infrared spectra of all the complexes of Tyr exhibit a broad and strong absorption at around 1490 cm^{-1} . These band may probably be due the $-\text{OH}$ group of the amino acid.

In agreement with analytical composition, the $[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{Cl}] \cdot 2\text{H}_2\text{O}$ and the $[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{Br}] \cdot 2\text{H}_2\text{O}$ exhibit infrared absorption bands at around 3210 cm^{-1} , characteristic of lattice water. In general water absorbs at $3550\text{--}3200\text{ cm}^{-1}$.

Electronic spectra

The UV-visible spectra of all the complexes show two absorption bands assigned to d-d transitions. The first, a broad band at $10800\text{--}15100\text{ cm}^{-1}$ region and the second is observed between 16700 and 21200 cm^{-1} . These absorption bands are characteristic of the octahedral cobalt (III) complexes with the low-spin d^6 configuration and can be assigned to a ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$ and ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$ transition, respectively [14, 15].

The spectral data in table 3 show that the variation of the position of the d-d transition bands is in agreement with spectrochemical series: $\text{I} < \text{Br} < \text{Cl} < \text{SCN}$, for the complexes of tyrosine. In all the complexes, additional band is located at around $32150\text{--}35500\text{ cm}^{-1}$ region, attributed to a charge transfer $\pi(\text{L}) \rightarrow d(\text{Co})$ transition [15].

In the $[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{X}]$ complexes, the field strength of the thiocyanato group, compared to these of X ($\text{X} = \text{Cl}, \text{Br}$ or I) is expected to be high. Indeed, it exhibits the highest field strength of 35500 cm^{-1} . The observed spectrochemical series of the Cobalt(III) complex ion is in the following increasing order: $\text{I} < \text{Br} < \text{Cl} < \text{SCN}$.

The energy of d-d transition for $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{NO}_2]$ compounds with Val and Thr as axial ligands increases in the order of ligand field: $\text{Val} < \text{Thr}$. The bands due to the charge transfer ligand-metal are shifted to lower energies in the same order of amino acids.

${}^1\text{H-NMR}$ Spectra

The ${}^1\text{H-NMR}$ spectral data for H_2dmg and the complexes are given in the table 4. In the spectra, the sharp singlet signal observed at 0.95 ppm for H_2dmg is shifted considerably down field in the complexes of Tyr to 2.34 ppm around, and to 2.38 ppm in the nitro complexes. This signal is due to the magnetically equivalent $-\text{CH}_3$ groups.

The $-\text{OH}$ (oxime) proton of free H_2dmg resonating at 10.40 ppm , undergoes also down field shift and appears in the complexes of Tyr at 11.40 ppm and in $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{NO}_2]$ ($\text{HA} = \text{Val}, \text{Thr}$) at 11.48 ppm . This important down field shifts of the protons in all these complexes is observed generally in the spectra of cobaloximes and supports the bonding of $-\text{NOH}$ groups through the nitrogen atoms to cobalt (III).

In the thiocyanato complexes the $-\text{CH}_3$ and $-\text{OH}$ protons signals are not well resolved.

The apparent inductive effect of X ligands on the shift of the $-\text{CH}_3$ resonance is relatively smaller for $[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{X}]$ complexes with $\text{X} = \text{Cl}, \text{Br}$ and I . For example, changing Cl by Br or I causes a shift of only $\sim 0.02\text{ ppm}$. However $-\text{CH}_3$ shifts seem rather sensitive to the steric effect of axial ligands. These conclusions have been obtained in ${}^1\text{H-NMR}$ studies on the alkyl and non alkyl cobaloximes [16].

The chemical analysis, and the spectroscopic studies predicts that the complexes synthesized correspond to the formulae $[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{X}]$ and $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{NO}_2]$. The Co(III) ion presents an octahedral configuration where two Hdmg bound in the equatorial positions. While the monodentate amino acid, SCN , NO_2 or halogenide ions are found in axial position. The structure is presented in figure 1.

Table 3: Electronic spectral data of Cobalt (III) complexes.

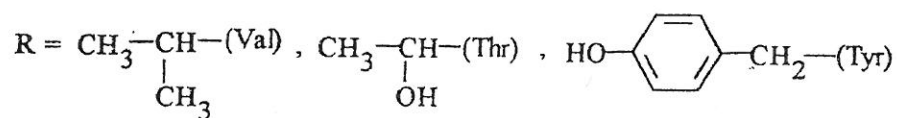
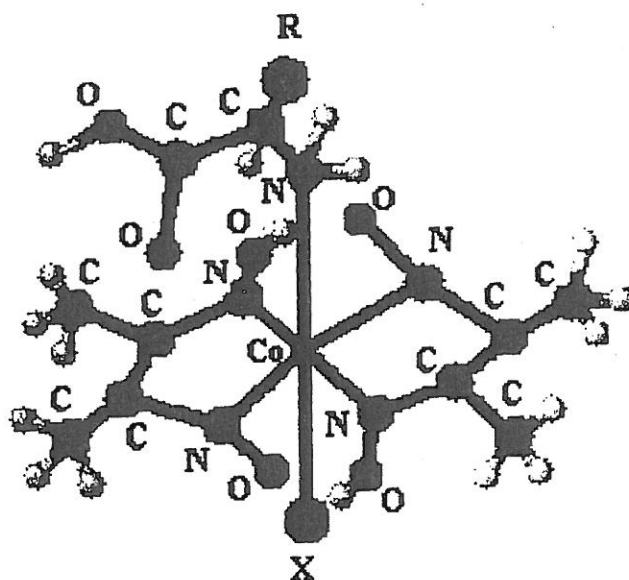
Compound	Electronic transition ^a (e) ^b		
	${}^1A_{1g} \rightarrow {}^1T_{1g}$	${}^1A_{1g} \rightarrow {}^1T_{2g}$	$\pi \rightarrow e_g$
[Co(Hdmg) ₂ (Tyr)Cl].2H ₂ O	15100 (11)	18250 (49)	34500 (20300)
[Co(Hdmg) ₂ (Tyr)Br].2H ₂ O	10950 (13)	17300 (77)	32450 (12770)
[Co(Hdmg) ₂ (Tyr)I]	10800 (35)	16700 (210)	32150 (18100)
[Co(Hdmg) ₂ (Tyr)SCN]	15100 (710)	-	35500 (10400)
[Co(Hdmg) ₂ (Val)NO ₂]	11260 (270)	16800 (350)	28000 (2820)
[Co(Hdmg) ₂ (Thr)NO ₂]	11760 (200)	21200 (200)	28100 (2500)

^aWave number in cm⁻¹^bAbsorption molar coefficient in mol⁻¹. L. cm⁻¹.

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Tableau 4: $^1\text{H-NMR}$ data of H_2dmg and complexes in DMSO-d_6

Complexe	$\delta (\text{CH}_3)$	$\delta (\text{OH})$
H_2dmg	0.95	10.40
$[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{Cl}] \cdot 2\text{H}_2\text{O}$	2.32	11.40
$[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{Br}] \cdot 2\text{H}_2\text{O}$	2.34	11.40
$[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{I}]$	2.34	-
$[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{SCN}]$	-	-
$[\text{Co}(\text{Hdmg})_2(\text{Val})\text{NO}_2]$	2.38	11.48
$[\text{Co}(\text{Hdmg})_2(\text{Thr})\text{NO}_2]$	2.38	11.48



$\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$ or NO_2

Figure 1: Suggested structure of the complexes.

Cyclic voltammetry.

The application of electrochemical methods to the study of the coordination of metal ions provides a useful complement to the previously used methods of investigation, such as UV-visible spectroscopy. Voltammetric behaviour of the complexes in DMSO was studied in the potential range from +1 V to -1.6 V.

The cyclic voltammograms of the iodo complex are characterized by five redox processes: I, II, III, IV and V, all the other complexes display four redox processes: I, III, IV and V. The first three processes (I, II and III) correspond to oxidations, whereas the redox systems (IV and V) appear to be associated with reduction processes. The redox potentials and the parameters, ΔE_p and i_{pa}/i_{pc} are listed in table 5 and the representative cyclic voltammogram of $[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{I}]$ complex is shown in Fig 2.

The electrochemical behaviour of the complexes resembles to that of other cobalt(III) complexes studied previously [3,17].

Complexes $[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{X}] \cdot n\text{H}_2\text{O}$ when $\text{X} = \text{Cl}, \text{Br}, \text{I}$ or SCN .

An oxidation waves (process I), observed between + 0.74 and + 0.92 V is well defined in the chloro and bromo complexes at nearly the same potential value as corresponding ligand (Hdmg) and can be attributed, to an irreversible oxidation of the Hdmg [17,18]. This wave (process I) is very weak in the iodo and thiocyanato complexes at all sweep rates. One oxidation wave corresponding to the process II ($E_{pa} = + 0.1$ V) characterize the chloro and bromo complexes. It is could be the result of the redox processes of the two halides. Whereas, in the voltammograms of the iodo and thiocyanato complexes two anodic processes (II and III) are observed. The first oxidation wave is displayed at + 0.2 V and the second, at + 0.5 V.

In the case of the iodo complex, this observation demonstrate that the two processes II and III are to be associated with the oxidation of the iodide ligand of the complexe. In fact, the iodide ion undergoes two successive oxidation steps [19].

Process IV revealed chemically irreversible pair voltammetric reduction-oxidation peaks of Co(III)/Co(II) redox couple centred at - 0.41; - 0.30 and - 0.25 V for the chloro, bromo and iodo complexes, respectively. While, for $[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{SCN}]$, the oxidation waves were very poorly resolved. For this series, the values of ΔE_p are between 140 and 210 mV at all sweep rates and the i_{pa}/i_{pc} ratio less of unity, evidenced this chemical irreversibility.

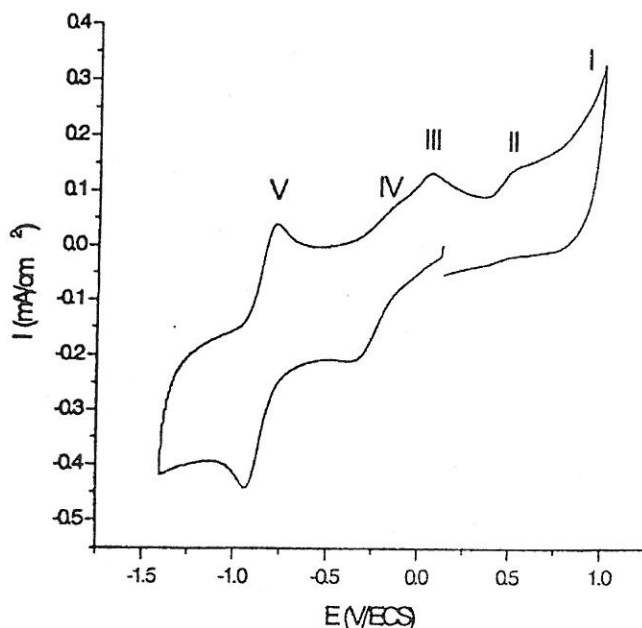


Figure 2 : Voltametric curve for $[\text{Co}(\text{Hdmg})_2(\text{Tyr})\text{I}]$ (1.10^{-3}M) at a glassy carbon disk electrode containing 0,1 M NaClO_4 at 20°C .

Table 5: Cyclic Voltammetric data of the complexes ($\sim 10^{-3}$ M) in DMSO containing ~ 0.1 M NaClO₄ at a Glassy Carbon electrode at 23°C.

Complexes	Cobalt redox couple	E _{pc} [V]	E _{pc} [V]	ΔE_p [mV]	I _{pa} /I _{pc}
[Co(Hdmg) ₂ (Tyr)Cl].2H ₂ O	Co (III) / Co (II)	-0.52	-0.31	210	-
	Co (II) / Co (I)	-0.95	-0.81	140	0.95
[Co(Hdmg) ₂ (Tyr)Br].2H ₂ O	Co (III) / Co (II)	-0.40	-0.20	200	-
	Co (II) / Co (I)	-0.95	-0.75	200	0.95
[Co(Hdmg) ₂ (Tyr)I]	Co (III) / Co (II)	-0.32	-0.18	140	-
	Co (II) / Co (I)	-0.94	-0.80	140	-0.95
[Co(Hdmg) ₂ (Tyr)SCN]	Co (III) / Co (II)	-0.33	-	-	-
	Co (II) / Co (I)	-0.94	-0.80	140	-0.90
[Co(Hdmg) ₂ (Val)NO ₂]	Co (III) / Co (II)	-0.70	-0.49	210	-
	Co (II) / Co (I)	-0.94	-0.82	120	1.0
[Co(Hdmg) ₂ (Thr)NO ₂]	Co (III) / Co (II)	-0.72	-0.50	220	-
	Co (II) / Co (I)	-0.95	-0.83	120	0.90

The Co(II)/Co(I) redox couple corresponding to the process V shows chemical reversibility because the ratio of the anodic peak current to the cathodic peak is nearly unity, but has a rather slow electron transfer ($\Delta E_p = 140 - 200$ mV). These electrochemical behaviours are similar to those reported previously [3,19].

A feature of the cyclic voltammetry of these complexes is the relative insensitivity of the Co(II)/Co(I) redox couple to the axial ligand [20,21]. The near invariance of the position of the cathodic peak corresponding to the reduction of Co(II) to Co(I) is consistent with the weak axial interactions in these cobalt(II) complexes which are considered to be five coordinate as observed by Endicott et al [23]. The near invariance of the position of the anodic peak corresponding to the oxidation of Co(I) to Co(II) is attributed to the complete loss of the axial ligands during the generation of the Co(I) complex [24,25].

Complexes $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{NO}_2] \cdot n\text{H}_2\text{O}$ when HA = Val or Thr.

The cyclic voltammetric behaviour of this group of complexes resembles to those of the complexes studied above. However, they undergo reduction from Co(III) to Co(II) at a less negative potential when compared to the halogeno or thiocyanato complexes. Upon, a wave corresponding to the reduction $\text{Co(III)} \rightarrow \text{Co(II)}$ is not well resolved for $[\text{Co}(\text{Hdmg})_2(\text{Val})\text{NO}_2]$ and $[\text{Co}(\text{Hdmg})_2(\text{Thr})\text{NO}_2]$ complexes. For the latter, the oxidation waves of Co(III)/Co(II) couple is also absent, confirming thus an irreversible character of the couple.

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