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Synthesis, Characterization, and Electrochemical Behavior of Mixed-Ligand Complexes of Cobalt(III) with Dimethylglyoxime and Some Amino Acids

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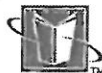
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ABSTRACT

The syntheses of non-electrolyte complexes of the general formula $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{X}]$, where Hdmg = dimethylglyoximate monoanion, HA = glycine (Gly), Serine (Ser), Cysteine (Cys) or Cystine (Cys–Cys)

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and $X = \text{Cl, Br, I, SCN}$ are described. The structure of the complexes proposed according to elemental analyses, IR, UV-Visible and ^1H NMR spectra is pseudo-octahedral. The cyclic voltammograms in DMSO at a GC disk electrode consist of two processes (I and II) corresponding to oxidations, whereas the redox systems III and IV appear to be associated with reduction processes. The Co(II)/Co(I) redox couple is reversible for various complexes and is relatively insensitive to the axial ligand. The Co(III)/Co(II) couple depends on the axial ligation, shows chemical irreversibility and has a much slower rate of electron transfer than the Co(II)/Co(I) couple due to the strong binding of the Lewis base to the Co(III) ion.

INTRODUCTION

The chemistry and the molecular structure of complexes of the type $[\text{Co}(\text{Hdmg})_2\text{RX}]$, called cobaloximes, (where $X = \text{Lewis bases}$, $\text{Hdmg} = \text{dimethylglyoxime monoanion}$, $R = \text{alkyl group}$) have been previously described.^[1-3] These compounds are interesting on one hand, because of their extensive coordination chemistry,^[4,5] and on the other hand, because of their relevance to the chemistry of vitamin B_{12} .^[6,7] As models for coenzyme B_{12} , cobaloximes have been subjected to extensive studies including their electrochemical^[8] and structural properties.^[9]

As part of our interest in the preparation of cobaloximes, we have previously reported the synthesis and studies^[10] of $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{X}]$ (where $\text{HA} = \text{alanine, threonine and histidine}$). As a continuation of our work on similar complexes, we have now extended this chemistry to the synthesis of a new series of cobalt(III) bis(dimethylglyoximato) complexes containing Gly, Ser, Cys and Cys-Cys as amino acid ligand and other halide or pseudo-halide ligands ($X = \text{Cl, Br, I, SCN}$). The synthesis, characterization and spectroscopic data for all these complexes are detailed below.

EXPERIMENTAL

Materials

All chemical reagents and solvents used in the synthesis of the complexes were Fluka p.a. grade products and were used without further purification. The amino acids used were: glycine (Gly), L(+)serine (Ser), L(+)cysteine (Cys) and L(-)cystine (Cys-Cys).

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Preparation of Complexes**Complexes $[\text{Co}(\text{Hdmg})_2(\text{Gly})\text{X}] \cdot 3\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$)**

To a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.38 g, 10 mmol) for the preparation of the chloro complexes or to a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.91 g, 10 mmol) in EtOH (30–40 mL) for the synthesis of all other complexes was added solid H_2dmg (2.32 g, 20 mmol) and amino acid (Gly) (0.75 g, 10 mmol). The mixture was stirred for 10 min. Solid NaBr (1.02 g, 10 mmol), NaI (1.50 g, 10 mmol) or KSCN (0.97 g, 10 mmol) was then added and air-oxidation was achieved by stirring vigorously in air for 45 min to 1 h 30 min. The complexes precipitated and were isolated by filtration, washed with EtOH, diethyl ether and dried in air.

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

These complexes were prepared as described above in 50 to 70 mL of EtOH and stirring for 2–3 h.

Complexes $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{SCN}]$ ($\text{HA} = \text{Cys}, \text{Cys-Cys}$)

These complexes were prepared as described above in 50 to 70 mL of aqueous EtOH (50% vol./vol.). The mixture was stirred for 3–4 h.

Physical Measurements

The elemental analyses were carried out at the Service Central d'Analyse du CNRS (Vernaison, France). Conductance values were obtained with a Tacussel CD-810 conductimeter at room temperature in $10^{-3} \text{ mol.L}^{-1}$ solutions of the complexes in DMSO. The IR spectra of solid samples (KBr discs) in the range $400\text{--}4000 \text{ cm}^{-1}$ were recorded on a Shimadzu FTIR-9101 M spectrophotometer. The electronic absorption spectra of solutions of the complexes in DMSO were recorded on a Shimadzu UV-1601 UV-Visible spectrophotometer in the range 250–950 nm. The ^1H NMR spectra were obtained with a Jed GSX 270 MSB (270 MHz) spectrophotometer in $\text{DMSO}-d_6$ solution for the complexes and for the dimethylglyoxime ligand, and in D_2O solution for the amino acid ligands, using TMS as internal reference (Service Commun de RMN, Université d'Angers). The electrochemical experiments were carried out using a 273-EGG potentiostat–galvanostat. A typical three-electrode cell was used. The



working electrode was a glassy carbon disc RDE (250 rpm); a platinum wire was the counter electrode, and silver wire immersed in electrolyte solution served as pseudo reference electrode. Both the reference electrode and the counter electrode were separated from the analyte solution by a fritted glass bridge. All solutions were deoxygenated by bubbling N_2 through the solutions for 15 min.

RESULTS AND DISCUSSION

The analytical data of the complexes are summarized in Table 1. Three series of complexes were obtained corresponding to the formulae $[Co(Hdmg)_2(Gly)X] \cdot 3H_2O$, $[Co(Hdmg)_2(Ser)X] \cdot nH_2O$ where $X = Cl, Br$ and $n = 2, 3$ or I and $[Co(Hdmg)_2(HA)SCN]$ where $HA = Gly, Ser, Cys$ or $Cys-Cys$. The molar conductance values of all complexes in DMSO at $10^{-3} \text{ mol.L}^{-1}$ are in the range $12-30 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and suggest that the complexes are non-electrolytes.

Infrared Spectra

The main IR bands of the ligands and their metal complexes are given in Table 2. The IR spectra of amino acids show no characteristic absorption bands assignable to the function NH_2 in the $3300-3500 \text{ cm}^{-1}$ range, they show the $\nu(NH_3^+)$ frequency in the $3150-3170 \text{ cm}^{-1}$ region.^[11] In glycine, cysteine and serine $\nu(NH_3^+)$ is observed at 3170, 3170 and 3150 cm^{-1} , respectively. The amino acids show a band in the $1660-1620 \text{ cm}^{-1}$ range. This band may be attributed to the NH_3^+ deformation.^[12] Two absorption bands corresponding to the asymmetric and symmetric modes occur in the ligands near 1575 around 1410 cm^{-1} that can be assigned to the ionic carboxyl of the acid moiety.^[12]

In the IR spectrum of H_2dmg , a band of medium intensity at 1447 cm^{-1} is assigned to the $\nu(C=N)$ vibration. The strong and sharp band appearing at 1444 cm^{-1} is due to the stretching vibration band of the $N-O$ group. The broad band at 750 cm^{-1} is attributed to $\delta(NOH)$ of the oxime part of the molecule.

In some cases, the characteristic IR absorption bands of the ligands are shifted to lower energy on complex formation and new bands, characteristic of the complexes, appear. The band of medium intensity occurring at around 3170 cm^{-1} corresponding to the $\nu(NH_3^+)$ frequency in the free amino acids series is shifted to 3100 cm^{-1} in the complexes. This is probably attributable to $\nu(NH_2^+)$. This band disappears in the serine com-



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Table 1. Analytical data of the complexes.

Compound formula	F.wt.	Colour	Yield (%)	Mp ^a (dec) (°C)	Found (calc.) (%)					
					C	H	N	Co	X ^b	H ₂ O ^c
[Co(Hdmg) ₂ GlyCl]·3H ₂ O	453.7	Brown	71	>205	26.6 (26.4)	5.0 (5.5)	15.5 (15.5)	13.6 (13.1)	—	11.6 (11.9)
C ₁₀ H ₂₅ ClCoN ₂ O ₉	498.1	Brown yellow	80	>200	23.7 (24.0)	4.5 (5.0)	13.9 (14.0)	11.4 (11.8)	—	10.4 (10.8)
[Co(Hdmg) ₂ GlyBr]·3H ₂ O	545.1	Brown	85	>200	21.8 (22.0)	4.1 (4.5)	13.1 (12.9)	10.7 (10.8)	23.7 (23.3)	9.6 (9.9)
C ₁₀ H ₂₅ BrCoN ₂ O ₉	465.7	Dark brown	36	>225	28.0 (28.3)	4.9 (5.3)	15.7 (15.0)	12.7 (12.6)	—	7.2 (7.7)
[Co(Hdmg) ₂ SerCl]·2H ₂ O	528.2	Light brown	57	>230	24.8 (25.0)	4.5 (5.1)	13.9 (13.3)	11.6 (11.1)	—	9.8 (10.2)
C ₁₁ H ₂₇ BrCoN ₂ O ₁₀	575.2	Brown	38	>225	22.4 (22.9)	4.1 (4.6)	12.4 (12.2)	10.9 (10.3)	—	8.8 (9.3)
[Co(Hdmg) ₂ Gly(SCN)]·3H ₂ O	476.3	Brown red	81	>210	27.4 (27.7)	4.8 (5.2)	17.9 (17.6)	12.0 (12.3)	7.4 (6.7)	11.0 (11.3)
C ₁₁ H ₁₉ CoN ₆ O ₆ S	452.3	Brown red	76	>240	31.3 (31.8)	4.0 (4.6)	18.1 (18.5)	13.3 (13.0)	7.7 (7.1)	—
[Co(Hdmg) ₂ Ser(SCN)]	468.4	Brown red	50	>235	30.8 (30.8)	4.9 (4.5)	18.1 (17.9)	13.0 (12.6)	13.0 (13.1)	—
C ₁₂ H ₂₁ CoN ₆ O ₆ S ₂	587.5	Brown	51	>240	31.1 (30.7)	4.8 (4.4)	16.1 (16.6)	9.4 (10.0)	16.2 (16.3)	—
[Co(Hdmg) ₂ Cys—Cys(SCN)]										
C ₁₃ H ₂₆ CoN ₇ O ₈ S ₃										

^aDecomposition starts at this temperature.^bX = Cl, Br, I or S.^cH₂O = lattice water (determined by heating at 110 °C and recording the weight loss).



Table 2. Main IR bands and their assignments.

Compound	$\nu(\text{NH}_3^+)$	$\delta(\text{NH}_3^+)$	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{sy}}(\text{COO}^-)$	$\nu(\text{C}=\text{N})$	$\nu(\text{NO})$	$\delta(\text{NO})$	$\nu(\text{Co}-\text{N})$	$\nu(\text{NCS})$
Gly	3170 s	1620 m	1560 w	1412 m	—	—	—	—	—
Ser	3150 s	1660 m	1578 m	1435 m	—	—	—	—	—
Cys	3170 m	1618 m	1575 w	1398 s	—	—	—	—	—
Cys-Cys	3170 m	1625 w	1575 m	1406 s	—	—	—	—	—
H ₂ dmg	—	—	—	—	1447 m	1144 s	750 m	—	—
[Co(Hdmg) ₂ GlyCl]·3H ₂ O	3142 s	1610 w	1574 s	1375 s	1445 w	1155 w	745 w	511 s	—
[Co(Hdmg) ₂ GlyBr]·3H ₂ O	3080 s	1638 s	1576 s	1385 s	1443 w	1158 w	745 w	511 s	—
[Co(Hdmg) ₂ GlyI]·3H ₂ O	3080 s	1630 w	1575 s	1385 s	1443 w	1149 w	758 w	511 s	—
[Co(Hdmg) ₂ SerCl]·2H ₂ O	—	—	1575 m	1375 s	1448 w	1150 w	760 w	509 s	—
[Co(Hdmg) ₂ SerBr]·3H ₂ O	—	—	1572 s	1375 s	1443 w	1154 w	755 m	509 s	—
[Co(Hdmg) ₂ SerI]·3H ₂ O	—	1636 w	1575 s	1380 s	1458 w	1150 w	755 b	511 s	—
[Co(Hdmg) ₂ Gly(SCN)]·3H ₂ O	3150 s	1638 w	1560 s	1385 s	1443 w	—	739 w	513 s	2145 s, 2178 s
[Co(Hdmg) ₂ Ser(SCN)]	3100 m	—	1557 s	1380 s	1447 w	—	739 s	513 s	2145 s, 2178 s
[Co(Hdmg) ₂ Cys(SCN)]	3125 s	1622 w	1564 s	1383 s	1408 w	1125 w	737 m	511 s	2143 s
[Co(Hdmg) ₂ Cys-Cys(SCN)]	3125 s	1622 w	1560 w	1380 w	1408 w	1149 w	737 s	511 s	2145 s

Abbreviations: s = strong, w = weak, m = medium.



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plexes. In this case, the bands may be masked by the $-\text{CH}$ group absorption. All amino acids show characteristic bands in the $1660\text{--}1610\text{ cm}^{-1}$ range^[12] and these vibrations are attributed to the NH_3^+ deformation. In coordination compounds, the deformation bands $\delta(\text{NH}_2^+)$ occur in the $1610\text{--}1338\text{ cm}^{-1}$ region. This absorption is not observed in all the serine complexes because it is probably associated with an asymmetric ionic stretching vibration band of the carboxyl, $\nu_{\text{as}}(\text{COO}^-)$.

The two absorption bands occurring near 1575 cm^{-1} and 1410 cm^{-1} in amino acids^[12] corresponding to the asymmetric and symmetric stretching vibration bands of the ionic carboxyl in the complexes, are shifted to lower frequencies, 1570 cm^{-1} , as broad bands and at 1380 cm^{-1} , as sharp bands, respectively. The IR spectra of the complexes suggest that the amino acids are coordinated through the nitrogen atom of the amino group.

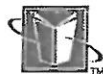
The $\nu(\text{C}=\text{N})$ frequency at 1447 cm^{-1} in free H_2dmg is observed at around 1445 cm^{-1} in the spectra of the complexes. This suggests that the ligand is coordinated to the metal ion through the nitrogen of the oxime.^[13] The appearance of a simple band at 1447 cm^{-1} in H_2dmg shows that the two oxime groups are identical while the appearance of a band for the complexes at around 1150 cm^{-1} , is assignable to $\nu(\text{NO})$. The sharp band occurring in the $737\text{--}760\text{ cm}^{-1}$ region in all the complexes is assigned to $\delta(\text{NOH})$. All the thiocyanato complexes exhibit a very strong and sharp band at around 2145 cm^{-1} assignable to the $\nu(\text{SCN})$ vibration.^[13]

The spectra of the complexes exhibit a new strong and sharp band at around 511 cm^{-1} which is not found in the spectra of the free ligands. In agreement with IR spectral studies on cobaloximes^[14,15] this band is assigned to $\nu(\text{Co}-\text{N})$.

All the complexes with glycine and serine show a broad band of strong intensity at 3540 cm^{-1} and in a few cases at around 3450 cm^{-1} , as excepted for $[\text{Co}(\text{Hdmg})_2(\text{Ser})\text{SCN}]$. It can be attributed to the $\nu(\text{OH})$ of water crystallisation. The IR spectra of $[\text{Co}(\text{Hdmg})_2(\text{Cys})\text{SCN}]$ and $[\text{Co}(\text{Hdmg})_2(\text{Cys}-\text{Cys})\text{SCN}]$ do not show the presence of water of crystallization molecules.

^1H NMR Spectra

The chemical shift of the methyl group of dimethylglyoxime (0.95 ppm) shifts considerably downfield in the complexes (to around 2.30 ppm) indicating that this ligand is coordinated through the nitrogen atoms. The dimethylglyoximate methyl group resonances are almost invariant across the series.^[16] The complexes and H_2dmg are only soluble in DMSO or



DMF, but the amino acids are not soluble in these same solvents. Thus, we have recorded the ^1H NMR spectra of the amino acids using D_2O solutions and all others in $\text{DMSO}-d_6$. It is not possible to compare the chemical shifts in different solvents; however, these spectra show unambiguously, in each case, that Hdmg coordinates through the nitrogen atoms.

Electronic Spectra

In DMSO solutions (around $5.10^{-3} \text{ mol.L}^{-1}$ for visible and $5.10^{-5} \text{ mol.L}^{-1}$ for UV spectra), the spectra of the complexes show two d-d transition bands and two bands due to ligand to metal charge transfer, all in the near-UV range. The positions of these bands and the molar absorption coefficients ϵ are given in Table 3.

The spectra in DMSO solution for the cobalt(III) complexes show two peaks of weak to moderate intensity at around $14,000\text{--}15,000 \text{ cm}^{-1}$ and $17,000\text{--}18,000 \text{ cm}^{-1}$ assignable to $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ transitions, respectively, typical of low-spin, six-coordinated cobalt(III) complexes.^[17] The variation of the position of the d-d transition bands agrees with the spectrochemical series: $\text{I} < \text{Br} < \text{Cl}$ for the halo complexes.

Unfortunately, the first d-d transition in the spectra of the thiocyanato series is not observed for all the complexes and it is not possible to classify the amino acids in increasing order of ligand field. For the thiocyanato complexes, the transition energies are quite identical. So, the amino acids involved in this series lead to an identical ligand field. This could be expected as these amino acids coordinate through the same atom: N from amino acid group.

Two additional bands appear in the range $20,500\text{--}26,000 \text{ cm}^{-1}$ and $29,500\text{--}33,000 \text{ cm}^{-1}$. These bands are due to ligand to metal charge transfer $\pi(\text{L}) \rightarrow \text{d}(\text{Co})$ transition. They are shifted to lower energies and this order follows the decreasing electronegativity of the halogens.

The analytical data and the spectroscopic studies show that these complexes are formulated as $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{X}]$. The Co(III) cation presents an octahedral geometry where the two Hdmg are bounded in the equatorial positions while the monodentate amino acid and the halogenide or the thiocyanate ions are located at the free axial positions. The structure is presented on Figure 1.

Electrochemical Behavior of the Complexes

The cyclic voltammograms of these complexes in DMSO consist in four redox processes labelled I, II, III and IV. A cyclic voltammogram of



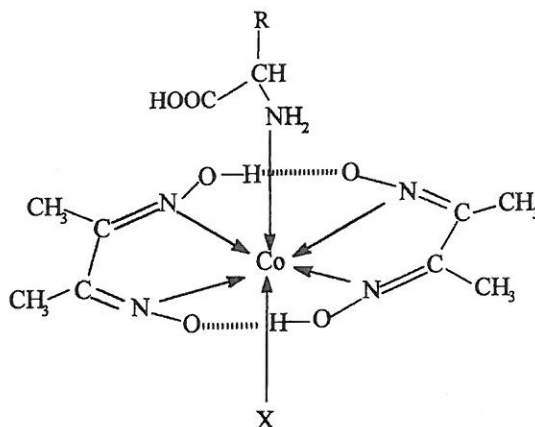
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Table 3. Electronic spectral data of cobalt(III) complexes.

Compound	Electronic transition ^a (ε) ^b		
	$^1A_{1g} \rightarrow ^1T_{1g}$	$^1A_{1g} \rightarrow ^1T_{2g}$	$\pi(L) \rightarrow d(\text{Co})$
[Co(Hdmg) ₂ GlyCl]·3H ₂ O	15,050 (19)	18,180 (71)	26,000 (1900)
[Co(Hdmg) ₂ GlyBr]·3H ₂ O	14,400 (30)	17,330 (116)	22,700 (2000)
[Co(Hdmg) ₂ GlyI]·3H ₂ O	14,085 (40)	17,095 (140)	22,320 (2340)
[Co(Hdmg) ₂ SerCl]·2H ₂ O	15,150 (23)	17,900 (85)	29,250 (2040)
[Co(Hdmg) ₂ SerBr]·3H ₂ O	14,450 (28)	17,540 (110)	21,980 (2600)
[Co(Hdmg) ₂ SerI]·3H ₂ O	13,700 (53)	17,420 (165)	21,930 (3080)
[Co(Hdmg) ₂ Gly(SCN)]·3H ₂ O	—	17,400 (140)	—
[Co(Hdmg) ₂ Ser(SCN)]	—	17,400 (130)	—
[Co(Hdmg) ₂ Cys(SCN)]	—	17,450 (75)	20,500 (470)
[Co(Hdmg) ₂ Cys-Cys(SCN)]	15,400 (17)	17,420 (30)	20,500 (410)

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



R = H (glycine); CH₂-OH (serine); CH₂-SH (cysteine);
H₂C-S-S-CH₂(NH₂)-COOH (cystine)

Figure 1. Suggested structures of the complexes.

[Co(Hdmg)₂SerCl]·3H₂O is shown in Figure 2. The cyclic voltammetric data for the oxidation and the reduction of the halo and thiocyanato complexes are presented in Table 4. The parameters, namely ipa/ipc and ΔE_p, used to evaluate the reversibility of the redox couples are given in the last two columns.^[18,19]

Processes I and II are oxidative while processes III and IV are reductive ones. On the basis of the results reported^[8,20] on the cobaloxime complexes, the assignment of the various redox sites of the Co(III) containing complexes studied show that the redox systems III and IV are metal-based and correspond to the successive reduction processes, Co(III)/Co(II) and Co(II)/Co(I). The values of the anodic peak potentials (E_{pa} = +0.86 V) and cathodic peak potentials (E_{pc} = +0.75 V) taken from the voltammogram of H₂dmg, compared with those obtained for the complexes, indicate that the oxidizing process I originates at the glyoximate moiety.

In order to identify the redox sites involved in the different oxidation steps, we have recorded the cyclic voltammograms of halide and thiocyanate salts under identical experimental conditions. Thus, the chloride, bromide and iodide salts undergo oxidation (E_{pa} ranging between +0.05 and +0.15 V). The reduction is observed only for the bromide and iodide salts at -0.15 and -0.05 V, respectively. Whereas the voltammogram of KSCN shows two waves corresponding to E_{pa} = -0.10 V and E_{pc} = -0.30

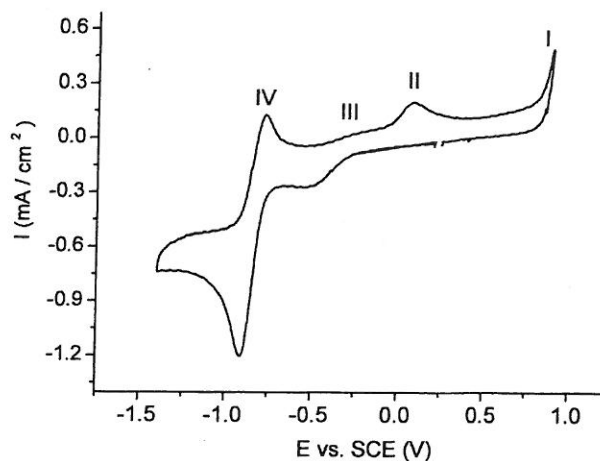


Figure 2. Cyclic voltammetric data for the reduction of $[\text{Co}(\text{Hdmg})_2(\text{Ser})\text{C}]\cdot 3\text{H}_2\text{O}$ (1.10×10^{-3} M) at a glassy carbon disc electrode containing 0.1 M NaClO_4 at 20 °C.

V at a scan rate of 300 mVs^{-1} . The waves corresponding to the redox system II, compared to those obtained for the salts may be attributed to the oxidation of the halide^[20] or thiocyanate ion. Similarly, it was mentioned that a wave due to the oxidation of a chloride ion is observed on the voltammogram of the complex $[\text{Co}(\text{Hdmg})_2\text{PyCl}]$.^[21]

Complexes $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{X}]\cdot 3\text{H}_2\text{O}$ (HA = Gly, Ser and X = Cl, Br, I)

In the case of these complexes, the oxidation processes I are irreversible as evidenced by the lack of a reduction wave during the reverse scan. The only anodic signal displayed by most of the complexes appearing at the potential $E_{\text{pa}} \approx +0.90$ V as process I can be attributed to the Hdmg ligand.^[8] Whereas the redox systems II show chemical reversibility ($\Delta E_p \sim 70\text{--}100$ mV) for the halo complexes. Voltammograms of salts containing Cl, Br, I and those of the complexes exhibits similar waves. This observation demonstrates that processes II corresponds to the oxidation of the halogens. For the Co(III)/Co(II) couple, the values of the anodic and cathodic peak potentials increase progressively in the following order of:



Table 4. Cyclic voltammetric data of complexes at a glassy disk electrode in DMSO containing NaClO₄ (0.1 M) at 20 °C.

Complex	Cobalt redox couple	E _{pc} (V)	E _{pa} (V)	ipa/ipc	ΔE _p (mV)
[Co(Hdmg) ₂ GlyCl]·3H ₂ O	Co(III/II) III	-0.46	-0.25	0.25	210
	Co(II/I) IV	-0.90	-0.79	0.76	110
Co(Hdmg) ₂ GlyBr]·3H ₂ O	Co(III/II) III	-0.41	-0.22	0.55	190
	Co(II/I) IV	-0.92	-0.79	0.95	130
[Co(Hdmg) ₂ GlyI]·3H ₂ O	Co(III/II) III	-0.40	-0.20	0.55	200
	Co(II/I) IV	-0.92	-0.80	0.96	120
[Co(Hdmg) ₂ SerCl]·3H ₂ O	Co(III/II) III	-0.50	-0.27	0.30	230
	Co(II/I) IV	-0.90	-0.78	0.85	120
[Co(Hdmg) ₂ SerBr]·3H ₂ O	Co(III/II) III	-0.41	-0.22	0.35	190
	Co(II/I) IV	-0.93	-0.80	0.95	130
[Co(Hdmg) ₂ Gly(SCN)]·3H ₂ O	Co(III/II) III	-0.46	-0.21	0.40	250
	Co(II/I) IV	-0.91	-0.79	0.70	120
[Co(Hdmg) ₂ Ser(SCN)]	Co(III/II) III	-0.44	-0.23	0.50	210
	Co(II/I) IV	-0.89	-0.79	0.96	100
[Co(Hdmg) ₂ Cys(SCN)]	Co(III/II) III	-0.53	-	-	-
	Co(II/I) IV	-0.92	-0.79	0.70	130
[Co(Hdmg) ₂ Cys-Cys(SCN)]	Co(III/II) III	-0.52	-	-	-
	Co(II/I) IV	-0.91	-0.78	0.98	130



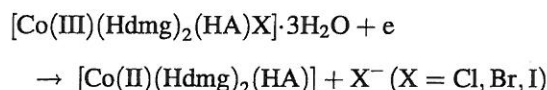
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It is seen in Table 4 that for the redox system III, the ratio of the anodic peak current to the cathodic peak current ranges between 0.25 and 0.55 indicative of the irreversibility of the Co(III)/Co(II) couple. The separation between the anodic and cathodic peak potentials, ΔE_p , is large, ranging from 190 mV to 250 mV at the sweep rate of 400 mV s^{-1} for the Co(III)/Co(II) redox couple, indicative of its electrochemical irreversibility.^[21] Also, both cathodic and anodic peaks of this couple lack the characteristic sharpness of a reversible electrode reaction. The values of the anodic and cathodic potentials in Table 4 show the sensitivity of the Co(III)/Co(II) couple to the nature of the axial ligand. This phenomenon is described in the electrochemistry of cobaloximes.^[8,15,21]

The anodic waves corresponding to the oxidation of Co(II) to Co(III) were poorly resolved, for the same couple, the cathodic peaks shift to potentials that are more negative with increasing sweep rate, confirming the character of an irreversible system.

The causes of the irreversibility may be attributed to extensive bond breaking during the reduction of the $[\text{Co(III)(Hdmg)}_2(\text{HA})\text{X}] \cdot 3\text{H}_2\text{O}$ complex. Thus, the axial ligand (X^-) is lost and the formation of a five-coordinate Co(II) complex is envisioned.^[18]



In the case of the Co(II)/Co(I) redox couple, the separation between the anodic and cathodic peak potentials span the 100–130 mV range at all sweep rates and the i_{pa}/i_{pc} ratio ≈ 0.75 –0.95, indicating the electrochemical reversibility of the couple. The observed insensitivity of the Co(II)/Co(I) couple to the nature of the various axial ligands also has been described in previous works on cobalt complexes.^[8,18,21] The invariance of the position of the cathodic peak corresponding to the process $\text{Co(II)} \rightarrow \text{Co(I)}$ is probably due to the weak axial interactions in these cobalt(II) complexes which are considered to be five-coordinate.

Complexes $[\text{Co(Hdmg)}_2(\text{HA})\text{SCN}]$ (HA = Gly, Ser, Cys and Cys–Cys)

The thiocyanato complex exhibits the same voltammetric behavior as does the halo complex. However, for these compounds only one anodic peak corresponding to the system II is well observed but the wave potentials E_{pc} are very poorly defined. Consequently, this redox system displays a lesser degree of reversibility than the halo complexes.



For the complexes of cysteine and cystine the waves corresponding to the oxidation of the Co(III)/Co(II) couple are not well resolved, confirming the irreversible character of the couple. The separation between the anodic and cathodic peak potentials, ΔE_p , is higher (210–250 mV) indicating a slow electron transfer for this couple.

When the complexes undergo reduction from Co(II) \rightarrow Co(I), the ratio $i_{pa}/i_{pc} \approx 0.96$ –0.98 indicates that the couple has chemical reversibility. Further, for the $[\text{Co}(\text{Hdmg})_2\text{CysSCN}]$ and $[\text{Co}(\text{Hdmg})_2\text{GlySCN}] \cdot 3\text{H}_2\text{O}$ complexes, the Co(II)/Co(I) couple exhibits poor reversibility ($i_{pa}/i_{pc} = 0.70$). In this case, a chemical reaction is probably coupled to the electrochemical reaction.

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