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The origin of optical activity in complexes of the type [Co(diimine)₂carbohydrate]²⁺

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Abstract

Complexes of the type Δ- and Λ-[Co(diimine)₂carbohydrate]²⁺ were synthesized with the diimines: 1,10-phenanthroline and 2,2′-bipyridine and with the carbohydrates: aminosugars, hexoses, pentoses and sucrose, with the aim of finding out which are the determining factors of the resultant chirality in these compounds. The optical characteristics of the complexes obtained were determined through measurement of their absorption and circular dichroism spectra. All the complexes synthesized exhibited an excitonic effect in the UV spectral region. Assignment of the circular dichroism bands in the visible could be performed by applying ligand field theory treatment and assuming a D_2 local symmetry to the optically active bands in the region of the d–d* absorption bands corresponding to the $^1A_1 \rightarrow {}^1B_2$ and $^1A_1 \rightarrow {}^1B_3$ transitions. Rotatory strength of these bands can be ascribed to coupling of the magnetic moments of the d–d* bands with the electric moments of the $\pi \rightarrow \pi^*$ transitions, polarized along the short axis of the diimine molecules, which turned out to be almost parallel in the Δ- and Λ-[Co(diimine)₂carbohydrate]²⁺ complexes.
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Keywords: Carbohydrate; Cobalt complex; Absorption spectra; Circular dichroism; Optical activity

1. Introduction

Carbohydrates, such as aminosugars: D-glucosamine, D-galactosamine, D-mannosamine; hexoses: D-glucose, D-galactose, D-mannose; pentoses: D- and L-arabinose, D- and L-xylose, D-ribose and sucrose (Scheme 1), react stereoselectively with the species Δ-, Λ-[Co(phen)₂Cl₂]⁺ with the exception of D-glucose (Table 1) [1–6]. The products thus obtained are of the type Δ- and Λ-[Co(phen)₂carbohydrate]²⁺, where the carbohydrate behaves as a bidentate ligand and is monodeprotonated. The chiral preference in the formation of these compounds may be caused by different structural factors, such as: interatomic distances, bonding angles, etc., leading to differences in the steric interactions of the diastereomers as a result of bigger or smaller distances
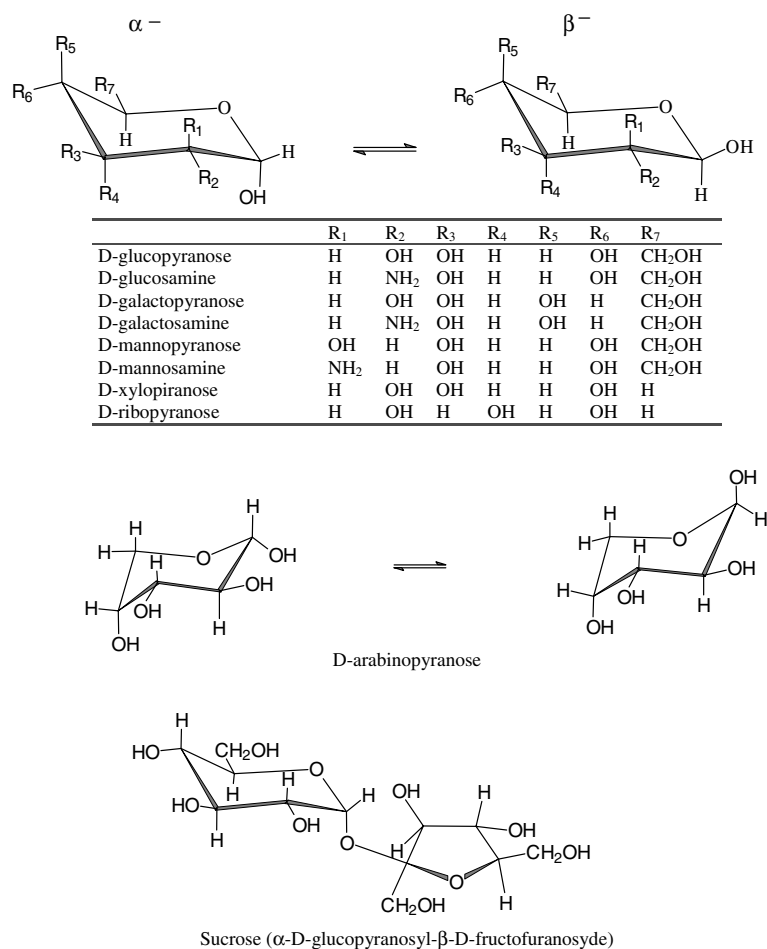
of the carbohydrate to the phenanthroline molecules in the coordination sphere (Fig. 1) [1–6]. The degree of stereoselectivity, though, does not change on replacing the phenanthroline ligands bipyridine (Scheme 2), in order to obtain compounds of the type Δ- and Λ-[Co(bipy)₂carbohydrate]²⁺. Results appearing in Table 2 [1] show that the higher degree of flexibility of the bipyridine molecule, compared to that of the phenanthroline, has no influence on the chiral preference in the process of formation of these complexes.

The monosaccharides, which adopt mainly the anomeric forms α or β, coordinate to the metallic ion through the ligand groups O⁻-1 and NH₂ or OH-2, adopting an axial, equatorial disposition or viceversa (Fig. 1) [1–5]. The coordinated anomer has one of the chair conformations: $^4C_1$ or $^1C_4$, slightly distorted, [7–9] compared to that of the free monosaccharide in water solution. On the other hand, coordination of the anomer (α or β) is independent of the nature of the aromatic diimine, thus coinciding with the independence of stereoselectivity with the nature of these ligands. Sucrose coordinates as a bidentate ligand,

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	R_1	R_2	R_3	R_4	R_5	R_6	R_7
D-glucopyranose	H	OH	OH	H	H	OH	CH_2OH
D-glucosamine	H	NH_2	OH	H	H	OH	CH_2OH
D-galactopyranose	H	OH	OH	H	OH	H	CH_2OH
D-galactosamine	H	NH_2	OH	H	OH	H	CH_2OH
D-mannopyranose	OH	H	OH	H	H	OH	CH_2OH
D-mannosamine	NH_2	H	OH	H	H	OH	CH_2OH
D-xylopiranose	H	OH	OH	H	H	OH	H
D-ribopyranose	H	OH	H	OH	H	OH	H

D-arabinopyranose

Sucrose (α-D-glucopyranosyl-β-D-fructofuranosyde)

Scheme 1.

Table 1
Preferred absolute configuration in complexes of the type [Co(phen)$_2$carbohydrate]$^{2+}$ and percentage of the Δ diastereomer

Complex	Preferred absolute configuration	Percentage of the Δ form[a]
[Co(phen)$_2$D-glucosamine]$^{2+}$	Δ	94
[Co(phen)$_2$D-galactosamine]$^{2+}$	Δ	95
[Co(phen)$_2$D-mannosamine]$^{2+}$	Δ	∼100
[Co(phen)$_2$D-galactose]$^{2+}$	Δ	∼100
[Co(phen)$_2$D-mannose]$^{2+}$	Δ	98
[Co(phen)$_2$D-glucose]$^{2+}$	$\Delta \approx \Lambda$	∼50
[Co(phen)$_2$D-arabinose]$^{2+}$	Δ	67
[Co(phen)$_2$D-ribose]$^{2+}$	Λ	37
[Co(phen)$_2$D-xylose]$^{2+}$	Λ	33
[Co(phen)$_2$D-sucrose]$^{2+}$	Δ	100

[a] The percentage values were obtained from the relation: $([\Delta]/([\Delta] + [\Delta])) \times 100$.

through the O$^-$-2 fragment of glucopyranose and through OH-1 of fructofuranose [6]. Conformation of coordinated sucrose does not change significantly compared to that of this ligand in its crystalline form [6].

The higher coordinating power of the amino group in the aminosugars [10] does not exert influence on the chiral preference nor on the degree of stereoselectivity of the resulting complexes [1]. In relation with this point, the complexes with aminosugars, as well as those with hexoses reach a higher degree of product with absolute configuration Δ during the synthetic process (Table 1). Besides, when the CH_2OH group in the position 5 of the hexopyranoses and of the aminohexopyranoses (Scheme 1) is replaced by an hydrogen atom, thus turning into a pentopyranose (Scheme 1), this last confers higher flexibility and higher entropy to the coordinated carbohydrate on both diastereomers [7–9], and the degree of chiral preference lowers (Table 1).

In complexes of the same type with the aminoalcohol "ephedrine", which shows a higher degree of flexibility than the carbohydrates, the products obtained do not show chiral preference [11]. Considering the evidence previously mentioned it is possible to correlate the "rigidity" [7–9] of the ligand with the degree of chiral preference in the systems here studied. Additionally, a direct relationship is observed between the size of the carbohydrate (Scheme 1) and the chiral preference. In this way,
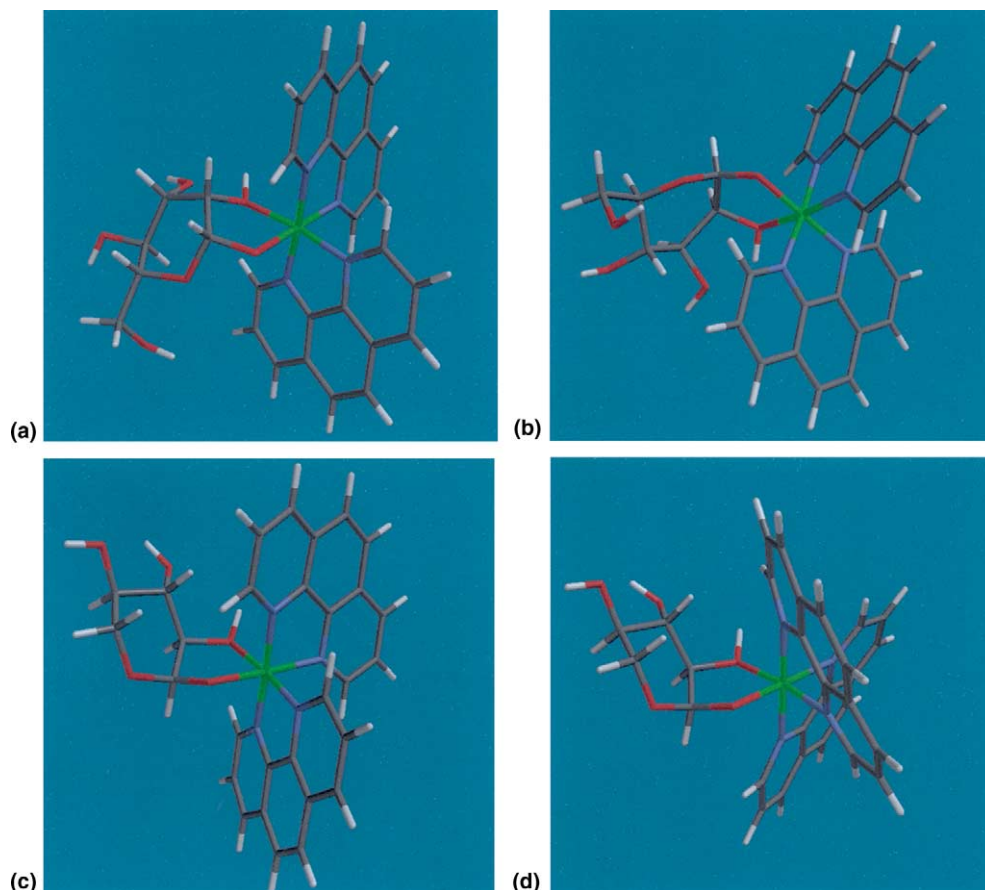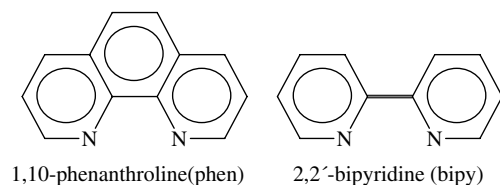
Fig. 1. The most likely structures of the complex ions: (a) Δ-[Co(phen)$_2$β-D-mannopyranose]$^{2+}$, (b) Λ-[Co(phen)$_2$β-D-mannopyranose]$^{2+}$, (c) Δ-[Co(phen)$_2$α-D-xylopyranose]$^{2+}$, (d) Λ-[Co(phen)$_2$α-D-xylopyranose]$^{2+}$, obtained with the semiempirecal PM3 (tm) method, SPARTAN program [26].

1,10-phenanthroline(phen)   2,2´-bipyridine (bipy)

Scheme 2.

Table 2
Preferred absolute configuration in complexes of the type [Co(bipy)$_2$carbohydrate]$^{2+}$

Complex	Preferred absolute configuration
[Co(bipy)$_2$D-glucosamine]$^{2+}$	Δ
[Co(bipy)$_2$D-galactosamine]$^{2+}$	Δ
[Co(bipy)$_2$D-mannosamine]$^{2+}$	Δ
[Co(bipy)$_2$D-galactose]$^{2+}$	Δ
[Co(bipy)$_2$D-mannose]$^{2+}$	Δ
[Co(bipy)$_2$D-glucose]$^{2+}$	Δ ≈ Λ
[Co(bipy)$_2$D-arabinose]$^{2+}$	Δ
[Co(bipy)$_2$D-ribose]$^{2+}$	Λ
[Co(bipy)$_2$D-xyilose]$^{2+}$	Λ

sucrose, which has a bigger size than the remaining carbohydrates here studied, can enter into the coordination sphere of the complexes Δ- and Λ-[Co(phen)$_2$Cl$_2$]$^+$ with a

minimum steric hindrance for the diastereomer of Δ configuration, which is formed exclusively [7]. From the previously mentioned evidence, it is possible to correlate the degree of stereoselectivity in the process of formation of the complexes Δ- and Λ-[Co(phen)$_2$carbohydrate]$^{2+}$ with both the rigidity of the ligand molecule and their relative size, according to the sequence [1]

sucrose > aminosugars ≈ hexopyranoses

> pentopyranoses.

This work covers also the study of the absorption and circular dichroism spectra of the complexes in terms of the "ligand-field" [12,13] and "perturbation" theories [14] in order to discover the origin of the optical activity in the visible spectral region.

2. Experimental

2.1. Synthesis of the bis-(diimine)(carbohydrate) Co(III) complexes

All the reagents and solvents used were p.a. and were used without further purification.

The complexes here synthesized, of the type bis-(diimine)(carbohydrate) cobalt(III), were prepared from complex salts of the general formula cis-[Co(diimine)$_2$Cl$_2$]Cl which, in turn, were obtained by the technique described by Ablov [15], to obtain cis-[Co(phen)$_2$Cl$_2$]Cl. This last compound, in our case, is the "precursor" complex. The same method was applied to obtain the precursor complex with 2,2′-bipyridine.

The compounds formed by Co(III), a carbohydrate molecule, and the previously mentioned diimines were obtained according to the following general procedure: 1 mmol of [Co(diimine)$_2$Cl$_2$]Cl and 2 mmol of a carbohydrate were mixed in 40 ml of water and the pH of the solution was adjusted to 8, with 0.1 M NaOH. The total volume was completed to 50 ml in a volumetric flask that was then sealed and introduced into a thermoregulated Haake K-F3 Model bath, where it was kept for one week at 25 °C. During that period the pH of the solution and its optical activity were controlled at intervals of 2 h in a Jobin Yvon CD-6 spectropolarimeter.

Once the maximum value of the optical activity was reached, the solution was transferred to an SP-Sephadex C25 chromatographic column (1 m long and 2 cm diameter) maintaining a speed of elution of 3 ml/min. The eluant used was NaCl in water in a gradient of 0.05–0.1 M concentrations. The fractions were gathered in an automatic collector (Advance SF-2120) and their circular dichroism and absorption spectra were recorded both in the visible as in the ultraviolet regions. The fractions showing the same sequence of optical activity signals were mixed in order to know the amount of complex through the concentration of cobalt. The fractions corresponding to the complexes of general formula Δ- and Λ-[Co(diimine)$_2$carbohydrate]$^{2+}$ showed a brownish colour in the case of the aminosugars and a red colour in the complexes formed by the hexoses,

pentoses and sucrose. In all these cases, yellow coloured products remained at the top of the column. They could be eluted with an NaCl 0.5 M solution. They corresponded to a racemic product, the complex [Co(diimine)$_3$]$^{3+}$ [16].

The complexes of Δ and Λ configuration, once isolated chromatographically, were precipitated with 0.1 M KI$_3$ as complex salts of this anion.

The solid products obtained were suspended in water and sonnicated, so as to remove the NaCl salt, that co-precipitated with the complex in the presence of the triiodide anion. The composition of the salts obtained was known through elemental analysis (Table 3). The compounds which do not appear in the table were only studied in solution.

2.2. Spectral measurements

Optical rotation measurements were performed in a Perkin–Elmer 141 spectropolarimeter, at 475 and 550 nm wavelength, at 25 °C in cells of 1 and 5 cm width.

The circular dichroism spectra were obtained in a Jobin Yvon CD-6 spectropolarimeter with 10^{-3}–10^{-4} M solutions of the complexes in the visible and 10^{-5}–10^{-6} M solutions in the ultraviolet spectral region, in quartz cells 0.1, 0.5 and 1 cm widths, in such a way as to have a maximum absorbance not greater than 0.8 absorbance units. Measurements of the absorption spectra were carried out in the same way as was described for the measurement of the circular dichroism, in the Jobin Yvon CD-6 and Unicam UV3 spectrophotometers, both in the visible and in the ultraviolet regions.

The cobalt content of the complexes in the solutions as in the solid compounds was found out by atomic absorption spectroscopy, with a Perkin–Elmer 1100B spectrophotometer.

Table 3
Elemental analysis of the complexes [Co(diimine)$_2$aminosugar](I$_3$)$_3$ and [Co(phen)$_2$carbohydrate](I$_3$)$_2$

Complex	% C	% H	% N	% Co
Δ-[Co(phen)$_2$D-glucosamine](I$_3$)$_3$	20.75(20.68)	1.65(1.67)	4.09(4.02)	3.50(3.39)
Δ-[Co(bipy)$_2$D-glucosamine](I$_3$)$_3$	18.80(18.43)	1.67(1.65)	4.25(4.13)	3.60(3.48)
Δ-[Co(phen)$_2$D-mannosamine](I$_3$)$_3$	19.65(20.68)	1.55(1.67)	4.14(4.02)	3.54(3.39)
Δ-[Co(bipy)$_2$D-mannosamine](I$_3$)$_3$	18.95(18.43)	1.63(1.65)	4.30(4.13)	3.72(3.48)
Δ-[Co(phen)$_2$D-galactosamine](I$_3$)$_3$	20.98(20.68)	1.78(1.67)	4.12(4.02)	3.56(3.39)
Δ-[Co(phen)$_2$galactose](I$_3$)$_2$	25.82(26.47)	2.04(1.99)	4.11(4.12)	4.20(4.23)
Δ-[Co(phen)$_2$mannose](I$_3$)$_2$	25.45(26.47)	1.82(1.99)	4.35(4.12)	4.00(4.23)
Δ-[Co(phen)$_2$glucose](I$_3$)$_2$	26.13(26.47)	2.07(1.99)	4.45(4.12)	4.32(4.23)
Δ-[Co(phen)$_2$sucrose](I$_3$)$_2$	28.43(28.38)	2.54(2.43)	3.81(3.68)	3.94(3.88)
Δ-[Co(phen)$_2$D-xylose](I$_3$)$_2$	26.00(26.17)	1.75(1.88)	3.94(4.21)	4.21(4.44)
Δ-[Co(phen)$_2$L-xylose](I$_3$)$_2$	26.39(26.17)	1.83(1.88)	4.48(4.21)	4.31(4.44)
Δ-[Co(phen)$_2$L-arabinose](I$_3$)$_2$	26.07(26.17)	1.60(1.88)	4.61(4.21)	4.00(4.44)
Λ-[Co(phen)$_2$L-arabinose](I$_3$)$_2$	26.47(26.17)	1.87(1.88)	4.36(4.21)	4.32(4.44)
Δ-[Co(phen)$_2$D-ribose](I$_3$)$_2$	26.65(26.17)	1.84(1.88)	4.46(4.21)	4.14(4.44)
Λ-[Co(phen)$_2$D-ribose](I$_3$)$_2$	25.98(26.17)	1.75(1.88)	4.37(4.21)	4.09(4.44)

Calculated values are inside parenthesis.
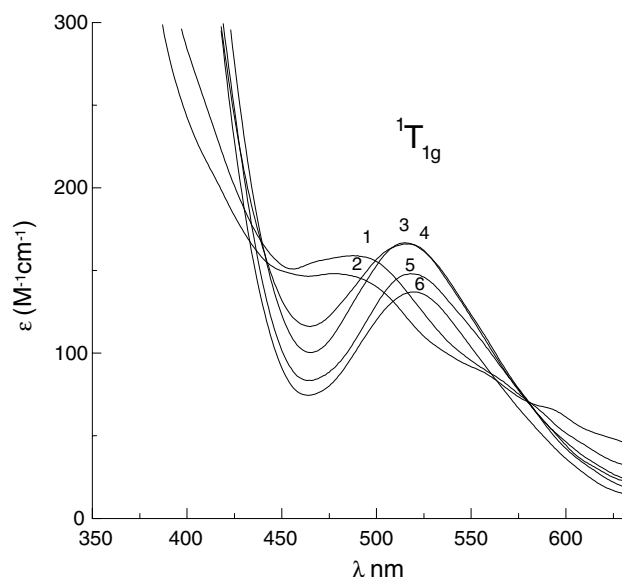
Fig. 2. Absorption spectra in the visible region of complexes Δ- and Λ-[Co(diimine)$_2$carbohydrate]$^{2+}$: (1) Δ-[Co(phen)$_2$D-galactosamine]$^{2+}$, (2) Δ-[Co(bipy)$_2$D-galactosamine]$^{2+}$, (3) Δ-[Co(phen)$_2$D-arabinose]$^{2+}$, (4) Δ-[Co(phen)$_2$D-galactose]$^{2+}$, (5) Λ-[Co(phen)$_2$D-glucose]$^{2+}$, (6) Δ-[Co(phen)$_2$sucrose]$^{2+}$.

Elemental analysis of C, H and N on the compounds synthesized were performed on a Fisons-Carlo Erba EA 1108 micro-analyzer.

3. Results and discussion

All of the Co(III) compounds formed by two molecules of an aromatic diimine and a carbohydrate, be it an aminosugar, an aldose (hexoses, pentoses) or sucrose, exhibit only one absorption band in the visible region (Fig. 2 and Tables 4–6) [1–6]. It is located in the region of 480–519 nm, corresponding to the $^1T_{1g}$ state in octahedral symmetry. This spectral range of absorption coincides with the expected one, according to the average field rule of the ligands [12,13,17,18], indicating, thus, that coordination of the aminosugar occurs through the NH$_2$ and OH groups. The remaining carbohydrates coordinate through two OH groups. On comparing the location of the $^1T_{1g}$ state of the complexes with aminosugars with that of complexes formed by the corresponding carbohydrates, it can be observed that the positions of the absorption band maxima are shifted ∼30 nm towards shorter wavelength (Fig. 2).

The energy level scheme included is a qualitative one and shows the sequence for octahedral (O$_h$) complexes of Co(III) and the resulting levels produced by rhombic distortion, assuming that they turn out to be ortho-axial, with holohedrized symmetry D_2 [16,24] (see Scheme 3). In regular octahedral complexes the Cartesian orbitals are split by symmetry in the e_g "class" that gives origin to σ bonds and the t_{2g} "class"

Table 4
Average values of absorption and circular dichroism for complexes Δ- and Λ-[Co(diimine)$_2$aminosugar]$^{2+a}$

	Absorption		CD	
	λ (nm)	log ε	λ (nm)	Δε (M^{-1} cm^{-1})
Δ-[Co(phen)$_2$D-aminosugar]$^{2+b}$	225sh	4.81	236	+9.5
	272	4.65	267	+13.3
			281	−19.4
	319sh	3.83	318	+4.0
	371.5sh	2.90	357	−1.2
	485	2.33	418	+1.2
			502	−2.8
			598sh	−0.13
Δ-[Co(bipy)$_2$D-aminosugar]$^{2+}$			260	+5.0
	305	4.23	299	+2.3
			319	−3.8
			337	+0.4
			353	−0.4
	482	2.10	424	+0.8
			501	−2.1
			599sh	−0.11
Λ-[Co(bipy)$_2$D-aminosugar]$^{2+}$			256	−3.45
	304	4.21	298.5	−2.15
			320.5	+2.25
			340.5	−0.55
			364	+0.14
	485	2.08	420.5	−0.4
			503.5	+1.2
			577sh	+0.35

[a] Diimines: 1,10-phenthroline and 2,2′-bipyridine and the D-aminosugars are: D-glucosamine, D-galactosamine and D-mannosamine.
[b] Values for D-glucosamine were published in [27]; those for D-galactosamine and D-mannosamine appear in [4].

Table 5
Average values of absorption and circular dichroism for complexes Δ- and Λ-[Co(diimine)$_2$carbohydrate]$^{2+}$[a]

	Absorption		CD	
	λ (nm)	$\log \varepsilon$	λ (nm)	$\Delta\varepsilon$ (M^{-1} cm^{-1})
Δ-[Co(phen)$_2$carbohydrate]$^{2+}$	226.7sh	4.9	228.5	−10.4
	270	4.65	267	+9.8
			280	−12.1
	324sh	3.75	322.5	+2.71
	357sh	3.22	364	−1.28
	517	2.21	414	+2.52
			512	−4.18
			608sh	−0.42
Λ-[Co(phen)$_2$carbohydrate]$^{2+}$	227sh	4.84	228	+9.2
	270	4.63	267	−8.8
			280	+10.6
	321sh	3.76	321	−2.9
	352.5sh	3.53	364	+1.1
	515	2.18	414	−2.37
			513	+3.85
			609sh	−0.25

[a] Carbohydrates are: D-galactose [5], D-mannose, D-glucose, D-, L-arabinose [5], D-, L-xylose, D-ribose and sucrose [6].

Table 6
Average values of absorption and circular dichroism for complexes Δ- and Λ-[Co(bipy)$_2$carbohydrate]$^{2+}$[a]

	Absorption		CD	
	λ (nm)	$\log \varepsilon$	λ (nm)	$\Delta\varepsilon$ (M^{-1} cm^{-1})
Δ-[Co(bipy)$_2$carbohydrate]$^{2+}$	305	4.28	270	+5.1
			315	−3.5
			329	+1.75
			363	−0.73
	510	2.16	407.5	+2.19
			504	−3.51
			600sh	−0.11
Λ-[Co(bipy)$_2$carbohydrate]$^{2+}$	303	4.26	270	−5.61
			316	+3.1
			326	−1.6
			358	+1.44
	508	2.15	411	−2.32
			505	+3.78
			605sh	−0.15

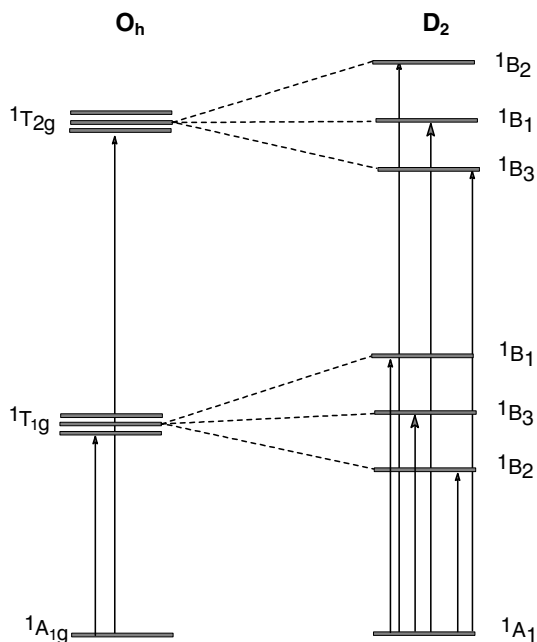[a] The carbohydrates are: D-galactose, D-mannose, D-, L-arabinose, L-xylose and D-ribose.

that forms π bonds. This classification can be applied to a Cartesian system of coordinates whose origin is placed at the nucleus of the central ion, in such a way that the axis addresses through the nuclei of the ligands. The chromophores that belong to this class are named orthoaxial. Holohedrized symmetry has been applied to such a structure where any interaction that takes place along the x, y and z axes is divided in halfs: one half addresses through $-x, -y, -z$, while the other half does it through x, y and z [16a,24]. On lowering the symmetry, three energy levels: $^1B_1$, $^1B_2$ and $^1B_3$ are expected for each singlet state of Co(III). Table 7 shows the three energy levels originating from the $^1T_{1g}$ and $^1T_{2g}$ octahedral levels on applying crystal field calculations [12,13]. The energy differences between

these levels are small and the observed spectral absorption band covers the three separate bands. The circular dichroism spectra, though, show two bands in this region.

Calculations of the rotatory strength based on the perturbation theory and considering D_2 symmetry show that only two out of the three transitions are optically active and of opposite signs. These last correspond to transitions between the fundamental, $^1A_1$ state to the $^1B_2$ and $^1B_3$ excited states.

These results coincide with the experimental evidence showing two circular dichroism signs in the region of the $^1T_{1g}$ state for each one of the complexes studied (Fig. 3).

Optical activity of the d–d transitions in the complexes Δ- and Λ-[Co(diimine)$_2$carbohydrate]$^{2+}$ may rise

Scheme 3.

Fig. 3. Absorption and circular dichroism spectra in the visible region of complexes Δ- and Λ-[Co(phen)$_2$carbohydrate]$^{2+}$: (1) Λ-[Co(phen)$_2$D-arabinose]$^{2+}$, (2) Δ-[Co(phen)$_2$D-galactose]$^{2+}$, (3) Δ-[Co(phen)$_2$D-arabinose]$^{2+}$, (4) Δ-[Co(phen)$_2$sucrose]$^{2+}$.

as the result of coupling of the magnetic moments in these transitions (m^*_{dd}) with the electric moments of the π–π^* transitions of the diimines (α band), that are polarized along the short axis of the diimine molecule ($\mu^*_{\pi\pi}$), both of which turn out to be parallel in all of the obtained compounds [14,19,20] and their rotatory strengths are of opposite signs.

Calculations of the energy levels of the complexes [Co(diimine)$_2$carbohydrate]$^{2+}$ having origin in the $^1T_{1g}$ state once split by rhombic distortion (D_2) (Table 7) give an average value of Dq$^{O^-}$ = 2033 cm^{-1}, corresponding to the splitting of the energy levels produced by the alcoxide group.

The calculated value for Dq$^{O^-}$ is similar to that of other Co(III) complexes, where the donor group is also O$^-$, as is the case for the oxalate or carbonate ions [17,21–24].
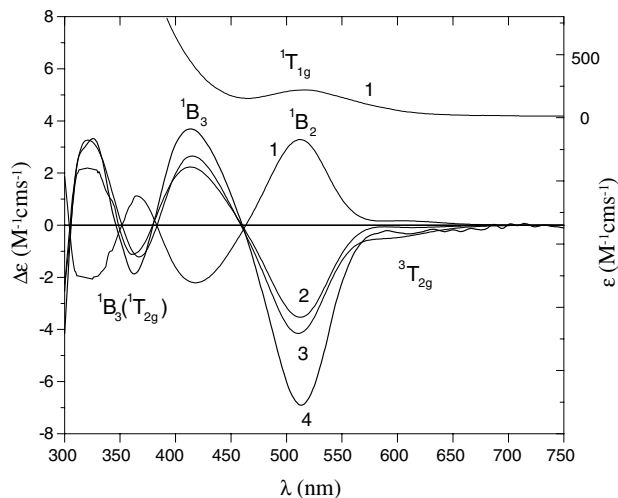
Regarding the absorption and circular dichroism bands in the zone of the d–d* transitions, the calculated energy level values for the Dq^{OH} parameter show an average of 2118 cm^{-1} for the complexes [Co(diimine)$_2$carbohydrate]$^{2+}$, (carbohydrate: hexoses, pentoses and sucrose). This value is also similar to those obtained for other Co(III) complexes with ligands coordinated through O$^-$ and OH, as is the case with H$_2$O [17,21–24]. Results indicate that the carbohydrates as ligands coordinate through the O$^-$ bonded to the carbon atoms 1 or 3 and through the NH$_2$ group bonded to the carbon atom 2 in the complexes with aminosugars. In complexes with sugars coordination is established through two OH groups, one of which is deprotonated.

Values obtained for B (Racah parameter) of d–d* transitions related to interelectronic repulsions (Table 8) are placed in the range of ~500 cm^{-1}. This value is in the order of magnitude of those calculated for other [CoN$_5$O$_1$] and [CoN$_4$O$_2$] systems [12,13]. It is generally

Table 7
Energies of transitions from the fundamental state $^1A_1$ to the excited state $^1B_1$, $^1B_2$ and $^1B_3$ (rhombic symmetry, D_2) for both $^1T_{1g}$ and $^1T_{2g}$ states

Complex[a,b]	$^1A_{1g} \rightarrow {}^1T_{1g}$ (cm^{-1})		
	$^1A_1 \rightarrow {}^1B_1$	$^1A_1 \rightarrow {}^1B_2$	$^1A_1 \rightarrow {}^1B_3$
[Co(diimine)$_2$aminosugar]$^{2+}$	20449(489)	20640(485)	20199(495)
[Co(diimine)$_2$carbohydrate]$^{2+}$	19336(517)	19432(515)	19931(502)
	$^1A_{1g} \rightarrow {}^1T_{2g}$		
	$^1A_1 \rightarrow {}^1B_1$	$^1A_1 \rightarrow {}^1B_2$	$^1A_1 \rightarrow {}^1B_3$
[Co(diimine)$_2$aminosugar]$^{2+}$	28156(355)	28059(356)	27809(360)
[Co(diimine)$_2$carbohydrate]$^{2+}$	28218(354)	28121(357)	28717(348)

[a] Diimines correspond to: 1,10-phenanthroline and 2,2′-bipyridine.

[b] Calculations did not consider the values of Ds, which are the same for all of these complexes, corresponding to 5/84 of the respective Dq values. Values inside parenthesis correspond to the wave lengths in nm.

Table 8
Spectral parameters in cm^{-1} obtained by measurements of the absorrtion and circular dichroism spectra of complexes [Co(diimine)$_2$carbohydrate]$^{2+a,b}$

Complex	$^1A_{1g} \rightarrow {}^3T_{2g}$ (cm^{-1})	$^1A_{1g} \rightarrow {}^1T_{1g}$ (cm^{-1})	$^1A_{1g} \rightarrow {}^1T_{2g}$ (cm^{-1})	B (cm^{-1})	C (cm^{-1})
[Co(diimine)$_2$aminosugar]$^{2+c}$	16682	20640	28396	485	3919
[Co(diimine)$_2$carbohydrate]$^{2+d}$	16584	19432	27950	532	3552

[a] The energy values, cm^{-1}, correspond to the average of the experimental values, both for complexes with aminosugars as for those with sugars, standard deviation: 110 cm^{-1}.

[b] Diimines corresponds to 1,10-phenanthroline and 2,2′-bipyridine.

[c] Aminosugars are: D-glucosamine, D-galactosamine and D-mannosamine.

[d] Carbohydrates are: D-glucose, D-galactose, D-mannose, D-, L-arabinose, D-, L-xylose, D-ribose and sucrose.

considered that the Racah parameter C (Table 8) reflects the radial expansion of the d orbitals in complexes [12,13]. Values of 3866 cm^{-1} were obtained for complexes with aminosugars and of: 3673, 3689 and 3682 cm^{-1} for complexes with hexoses, pentoses and sucrose, respectively.

Comparison of the values 3873 cm^{-1} for [Co(NH$_3$)$_4$C$_2$O$_4$]$^+$ and 3720 cm^{-1} for [Co(NH$_3$)$_4$CO$_3$]$^+$ [12,13,25] shows that expansion by delocalization towards the ligands via π system is relatively unimportant in these cases.

In the present work the absolute configurations Δ and Λ of complexes [Co(diimine)$_2$carbohydrate]$^{2+}$ were identified by their circular dichroism spectra, according to the sign sequence of the "excitonic" effect [18] of the $\pi \rightarrow \pi^*$ transition at $\sim$270 nm for compounds with phenanthroline and of $\sim$300 nm for complexes with 2,2′-bipyridine (p band) [16], in the complexes having two diimine molecules as ligands (Fig. 4, Tables 4–6). The "excitonic" effect [18] consists of the presence of two

Fig. 4. Absorption and circular dichroism spectra in the UV region of complexes Δ-[Co(phen)$_2$carbohydrate]$^{2+}$: (1) D-mannosamine, (2) sucrose [6], (3) D-galactose [5], (4) D-arabinose [5] and (5) Λ-[Co(phen)$_2$D-arabinose]$^{2+}$ [5].

circular dichroism bands of opposite signs under the p absorption band, as a result of electrostatic coupling of the dipolar moments of the electric transitions in the individual diimine ligand molecules in these type of complexes. Besides the previously mentioned signals, a circular dichroism band is observed in the UV region, localized in the range of 241–243 nm (β band), that should correspond to a transition polarized along the major axis of the diimine molecule and calculated by self consistent field [13] to be at 260 nm. The corresponding absorption band is generally masked. The band of phenanthroline appears as a shoulder at $\sim$320 nm in the absorption spectrum and gives a neat circular dichroism band at this wavelength (Fig. 3).

This last band is overlapped by the "p" band in the absorption spectra of the complexes [Co(bipy)$_2$carbohydrate]$^{2+}$. In the circular dichroism spectra, though, it can be observed at $\sim$340 nm (Tables 4–6).

Correlation among the circular dichroism spectra in the visible region and configuration around Co(III) in the *tris*-chelate complexes is based on the location of the $^1A_2$ and ^1E states in D_3 symmetry (or $^1B_1$, $^1B_2$ and $^1B_3$ in the systems of D_2 symmetry), corresponding to the first excited state [14,19]. It has been found that the transition of ^1E symmetry shows a positive circular dichroism signal, whereas, in that of $^1A_2$ symmetry, the signal is negative when the complex has a Λ configuration (the signs will be the apposite ones for a complex of Δ configuration). It has to be born in mind also that the signal corresponding to the ^1E transition is always more intense than that of the $^1A_2$ transition, making it possible to identify them in the corresponding spectrum [17,21–24]. In the complexes of the type [Co(diimine)$_2$AB], where AB is a bidentate ligand, one of the components of the first excited state, the one deriving from the ^1E state in D_3 symmetry ($^1B_2$ under D_2 symmetry), dominates the circular dichroism spectrum. This is the one responsible for the positive or negative Cotton effect in the circular dichroism curve in the visible region, and is correlated with the absolute configuration of the *tris*-chelate Co(III) complex [1,18,21–24].

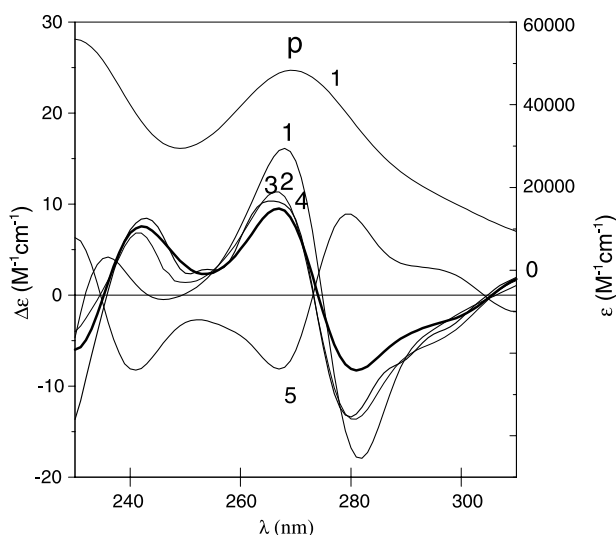In all of the circular dichroism spectra examined, whose configuration has been known through the exci-

tonic effect, it can be seen that the first signal in the visible spectra is located at 502–513 nm. This is the band showing higher rotatory strength (higher $\Delta\varepsilon$) and has a negative sign in the complexes of Δ configuration and a positive sign for those of Λ configuration (Fig. 3 and Tables 4–6). This band corresponds to the $^1A_1 \rightarrow {}^1B_2$ transition under D_2 symmetry, according to the calculated rotatory strength for the complexes [14,19,20]. The band located at 410–415 nm has a lower $\Delta\varepsilon$ value, is of opposite sign to that of the previously mentioned one and it should correspond to the $^1B_3$ state under D_2 symmetry. It was assigned, as it was previously described [14,19,20]. In all of these complexes the states $^1B_3$ and $^1B_2$ in D_2 symmetry (region of the $^1T_{1g}$ state in O_h symmetry) are those that coincide with the sign sequence of the excitonic effect and, consequently, with the absolute configuration of the complexes [13,21]. Under the first absorption band in the visible region, corresponding to the $^1T_{1g}$ state there are two circular dichroism signals of opposite signs (Fig. 3 and Tables 4–6) under the first absorption band in the visible region, corresponding to the $^1T_{1g}$ state. The two circular dichroism signals arise from the partition of the $^1T_{1g}$ state of Co(III) under rhombic distortion, as a result of coordination of two molecules of an aromatic diimine plus one molecule of a carbohydrate around the metallic ion (Table 7) [12,13].

The p and α bands of the aromatic diimine overlap part of the absorption spectrum of Co(III) in all the Δ- and Λ-[Co(diimine)$_2$carbohydrate]$^{2+}$ complexes. Nevertheless, the corresponding circular dichroism spectra reveal a clear signal at $\sim$364 nm. (Fig. 3 and Tables 4–6), that can be assigned to the $^1T_{2g}$ state in octahedral symmetry and, under D_2 symmetry, it would correspond to the transition from the fundamental $^1A_1$ state to the $^1B_3$ excited state [14,19,20]. The transition from the $^1A_1$ to the $^1B_2$ state in this region is expected to show optical activity of opposite sign to that of the $^1B_3$ state. This point could not be checked experimentally, since in the complexes Δ-, Λ-[Co(phen)$_2$carbohydrate]$^{2+}$ (Fig. 3, Tables 6–8) the circular dichroism spectra of these bands are overlapped by the α band, whereas in the complexes Δ- and Λ-[Co(bipyridine)$_2$carbohydrate]$^{2+}$ they are overlapped by the p and α bands (Table 6).

It could be observed also that the $^1A_1 \rightarrow {}^1B_1$ transition is not optically active in these complexes [14,19,20]. This result is in agreement with the number of signals of these compounds in the region of the $^1T_{2g}$ state [1–6].

In the circular dichroism spectra of the Δ and Λ isomers examined, a weak signal appears at the lower energy side of the $^1T_{1g}$ state band, that can be isolated by gaussian analysis: its location and $\Delta\varepsilon$ value lead to associate it to the $^3T_{2g}$ state of Co(III) in the complexes (Fig. 3 and Tables 4–6). Location of this spectral signal coincides with that of spin-forbbiden bands in Co(III) complexes with a similar coordination sphere [17,21].

Summarizing, it is worthwhile to remark the following features for the type of complexes here studied.

The circular dichroism spectra of the complexes show remarkable regularity in the number of spectral bands, sign sequence and intensity of the signals, independently of the nature of the carbohydrate ligands, number of asymmetric centers present in the chiral ligands; distribution of the asymmetric centers (R or S) of the C atoms bonded to N or O atoms that establish coordination, nor the conformation of the ring around the metallic ion. The same can be said about the different aromatic diimines 1,10-phenanthroline and 2,2′-bipyridine.

The spectra of the complexes here studied make it possible to spot the circular dichroism bands corresponding to singlet–triplet electronic transitions, which are rarely observed.

It is also worthwhile remarking that the carbohydrates as ligands, when bonded to Co(III) and form *tris*-quelate complexes with a particular configuration, make it possible to observe, as few other ligands do, the majority of the electronic transitions of this ion.

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