# ISOLATION AND CHARACTERIZATION OF COBALT (III) TRIS-D-AMINOSUGARS

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## ABSTRACT

Mixed complexes of aminosugars and 1,10-phenanthroline (phen) with cobalt(III), with the composition $Co(III)(phen)_2$sugar, disproportionate in aqueous solution in approximately one month, giving non ionic tris-aminosugar complexes. The complexes with $\alpha$-D-glucosamine, $\alpha$-D-galactosamine and $\beta$-D-mannosamine have the L-configuration at Co(III) with facial isomerism, on the bases of molecular composition and absorption and circular dichroism spectra.

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## 1. INTRODUCTION

Sugars and related polyols exhibit a rich chemistry in forming a variety of complexes with metal ions [1]. Mixed complexes involving a sugar and another ligand, e.g., a diamine, have also been characterized. We have identified mononuclear complexes of sugars and 1,10-phenanthroline (phen) with cobalt(III), with the composition Co(III)(phen)$_2$sugar [2-4]. The configuration at Co(III) is given by the circular dichroism (CD) or optical rotatory dispersion (ORD) spectra [2,3] and NMR spectroscopy provides additional information on conformation and carbohydrate-metal ion bonding sites [4].

The mixed complexes of bis-phenanthroline Co(III) with aminosugars disproportionate in approximately one month, giving non ionic tris-aminosugar complexes and tris-phenanthroline Co(III) [5]. The sugar ligands used were: $\alpha$-D-glucosamine, $\alpha$-D-galactosamine, and $\beta$-D-mannosamine.

## 2. EXPERIMENTAL

The compounds $\Delta$- and L-[Co(phen)$_2$carbohydrate]$^{2+}$, synthesized as in the literature [2-4], were left in aqueous solution for approximately one month at ca. 25 ºC and were then transferred to a chromatographic column of SP-Sephadex C25, 35 cm length and 2 cm diameter, at a flow rate of 3 ml / min. The eluant was aqueous NaCl in a concentration gradient between 0.02 and 0.1 M. Fractions were collected with an automatic collector and circular dichroism and absorption spectra were monitored in the visible region. The amino sugar was eluted first. Then came two coloured fractions: one yellow, of the racemic complex [Co(phen)$_3$]$^{3+}$ [6], and the other, dark violet, of a nonionic chiral tris-aminosugarCo(III) complex, was characterized by its absorption and circular dichroism spectra. For the product of decomposition of D-[Co(phen)$_2$D-glucosamine]$^{2+}$ the solution was evaporated to dryness and the solid was then extracted and recrystallized several times with MeOH to eliminate NaCl and its composition was determined by elemental analysis.

Microanalysis of [Co($\alpha$-D-glucosamine)$_3$]·5H$_2$O gave: Co 8.51 %(8.64); C 31.0 % (31.63) ; N 5.98%(6.15);H 6.52%(6.73). Predicted values are in parentheses.

The results show that the three D-glucosamine ligands are monodeprotonated. The other complexes with aminosugars have similar patterns of absorption and circular dichroism bands as the tris-D-glucosamine complex, and with absorption at ~550 nm due to the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition under octahedral symmetry (Figs. 1-3 and Table 1). The location of this absorption band is related to Co(III) surrounded by three nitrogen and three oxygen atoms [CoN$_3$O$_3$] [7]. The products of disproportionation of the other aminosugar complexes follow this pattern.
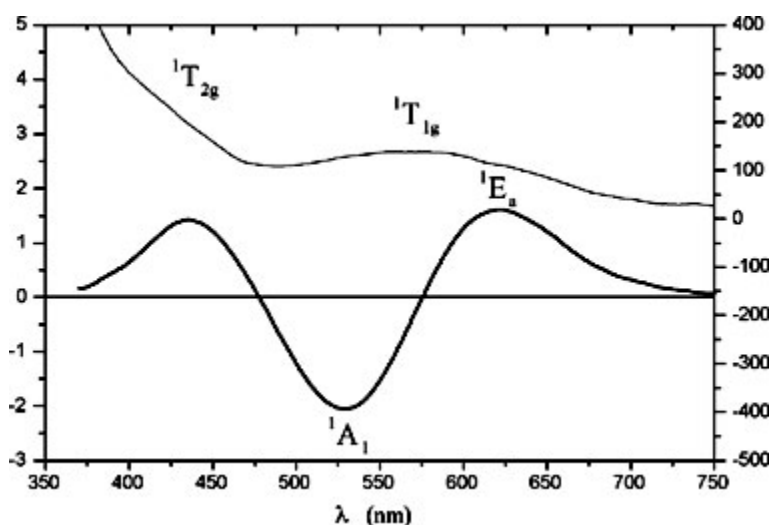


**Fig. 1.** Absorption spectra and circular dichroism
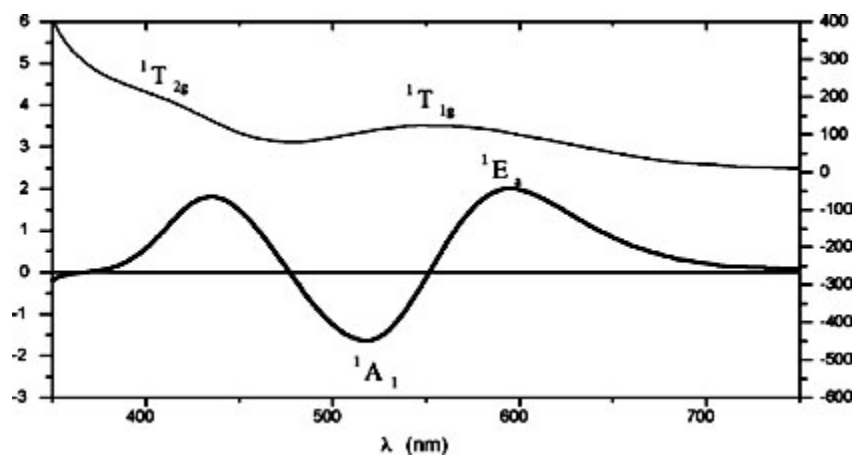
spectra of L-[Co($\alpha$-D-glucosamine)$_3$].



**Fig. 2.** Absorption spectra and circular dichroism spectra of L-[Co($\alpha$-D-galactosamine)$_3$].
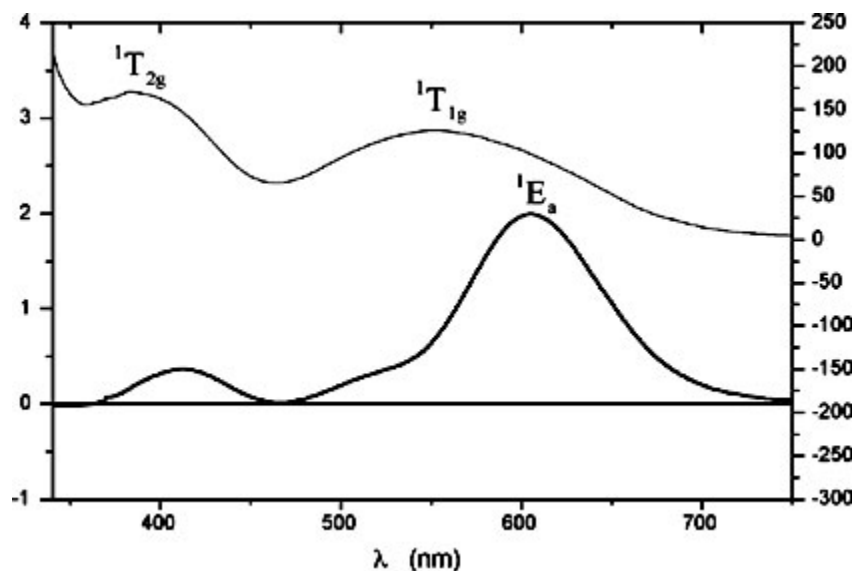


**Fig. 3.** Absorption spectra and circular dichroism spectra of L-[Co($\beta$-D-mannosamine)$_3$].

**Table 1.:** Values of absorption and circular dichroism for complexes L-[Co(D-aminosugar)$_3$]

| Aminosugar Ligand | ABSORPTION | CD |
|---|---|---|

$\Delta\varepsilon$ (M$^{-1}$cm$^-$

|  | $\lambda$ (nm) | log $\varepsilon$ | $\lambda$ (nm) | [1]) |
|---|---|---|---|---|
| D-glucosamine | 420sh | 2.47 | 435 | +1.4 |
|  | 568 | 2.13 | 529 | -2.0 |
|  |  |  | 622 | +1.6 |
| D-galactosamine | 410sh | 2.27 | 435 | +1.8 |
|  | 548 | 2.09 | 518 | -1.6 |
|  |  |  | 595 | +2.0 |
| D-mannosamine | 388sh | 2.27 | 410 | +0.4 |
|  | 552 | 2.09 | 505sh | -0.3 |
|  |  |  | 605 | +2.0 |

## 2.1 Spectral measurements

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 spectral region, in 0.5 and 1 cm cuvettes, with a maximum absorbance < 0.8 units. Measurements of the absorption spectra were carried out as for the that of circular dichroism, in the Jobin Yvon CD-6, or in a Unicam UV3 spectrophotometer in the visible region.

The cobalt content of the complexes in solutions or the solid, was estimated by atomic absorption spectroscopy, with a Perkin Elmer 1100B spectrophotometer.

Elemental analyses of C, H and N on synthesized tris-glucosamine Co(III) complex samples were made on a Fisons-Carlo Erba EA 1108 micro-analyzer. For other tris-aminosugar Co(III) complexes it was not possible to determine their elemental composition because they rapidly disproportionate.

## 2.2. NMR spectroscopy

The $^1$H NMR spectra of the tris-aminosugar Co(III) complexes were obtained with isolated chromatographic fractions after air drying and storage in a $CaCl_2$ desiccator. The $^1$H NMR spectra in $D_2O$ were measured in a Bruker DRX 300 instrument.

The $^1$H NMR signals in the anomeric region were observed and compared with those of the free sugar (Table 2). A small amount of Co(II) produced in the disproportionation broadens the signals, and in some systems it was not possible to determine the coupling constants. In addition there was interference by signals of the free sugars formed by decomposition of these labile complexes.

**Table 2.**

[1]H Chemical shifts, (d, ppm) and coupling constants, (J, Hz) in the anomeric region of free and coordinated α- or β-D-aminosugars [a]

| Aminosugar | $\delta$ (ppm) | $^3J_{1,2}$ (Hz) |
|---|---|---|
| Co(III)(a-D-glucosamine)$_3$ | 5.44 | 3.5 |
| D-glucosamine α | 5.22 | 3.5 |
| D-glucosamine β | 4.58 | 8.0 |
| Co(III)(a-D-galactosamine)$_3$ | 5.39 | 4.0 |
| D-galactosamine α | 5.28 | 4.0 |
| D-galactosamine β | 4.53 | 8.0 |
| Co(III)(b-D-mannosamine)$_3$ | 4.50 | [b] |
| D-mannosamine α | 5.17 | 1.5 |
| D-mannosamine β | 5.00 | [b] |

[a] Referred to TSP, $\delta$ = 0. [b] broad signal.

## 3. Results and discussion.

The three aminosugar complexes have absorption and CD signals at ca. 550 nm., due to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition, characteristic of low symmetry octahedral complexes with three bonded nitrogens and three bonded oxygens [7] (Figs 1-3 and Table 1).

For complexes with a-D-glucosamine and α-D-galactosamine there are two CD signals of opposite sign, related to the $^1A_{1g}$ and $^1E_a$ states of Co(III) under C$_3$ microsymmetry, with facial isomerism [6,7] (Figs 1 and 2). The absorption spectra have shoulders at ca. 400 nm, corresponding to $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions with positive CD signals. As expected for this type of isomerism [6], in [Co(aminoacidate)$_3$] complexes there are changes of sign sequence in such maxima from negative to positive with variation of the wave length [6,7], this sequence shows that the absolute configuration of these Co(III)carbohydrate complexes is L at Co(III).

The sign sequence differs for the β-D-mannosamine complex, with positive CD in the region of the $^1T_{1g}$ state of Co(III), a strong signal at 605 nm, and a shoulder at 505 nm. The first signal is related to the $^1E_a$ state, with L configuration for this complex [6,7].

The ^{1}H NMR spectra of the $\Lambda$-[Co(D-glucosamine)$_3$] and $\Lambda$-[Co(D-galactosamine)$_3$] complexes in D$_2$O show in the anomeric region, in addition to signals of the free aminosugar doublets with chemical shifts of 5.44 ppm and 5.39 ppm, respectively, and coupling constants of 3.5 Hz and 4.0 Hz, corresponding to the H-1 signals of the coordinated aminosugars in the respective complexes (Table 2). In these complexes the aminosugars should coordinate to Co (III) as $\alpha$- anomers, through the axial O$^-$-1 and equatorial NH$_2$ as in the corresponding D- and $\Lambda$-[Co(phen)$_2$ $\alpha$-D-aminosugar]$^{2+}$ complexes [2,3].

The ^{1}H NMR spectrum in the anomeric region of the $\Lambda$-[Co(D-mannosamine)$_3$] complex has some signals of the free sugar and a signal at 4.50 ppm of the L-[Co(D-mannosamine)$_3$] complex (Table 2). A chemical shift ~4.1 ppm is characteristic of a D- or $\Lambda$-[Co(phen)$_2$ $\alpha$-D-aminosugar]$^{2+}$ complex [2,3] with the axial H-1 of the sugar and coordination to Co(III) through the equatorial O$^-$-1. D-Mannosamine coordinates to Co(III) as a bidentate ligand in the $\beta$ anomeric form, through the equatorial O$^-$-1 and axial NH$_2$. This evidence is consistent with the location of the visible absorption band of the complex.

In conclusion, the tris-aminosugar Co(III) complexes, synthesized in solution, show optical activity with C$_3$ microsymmetry and the coordination sphere is CoN$_3$O$_3$. The anomeric aminosugar in these $\Lambda$-tris-aminosugar Co(III) complexes is $\alpha$- for the D-glucosamine and D-galactosamine and $\beta$- for the D-mannosamine complexes. In all cases the adjacent groups O$^-$-1 and NH$_2$ are in axial conformations.

## ACKNOWLEDGEMENTS

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