

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

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## ABSTRACT

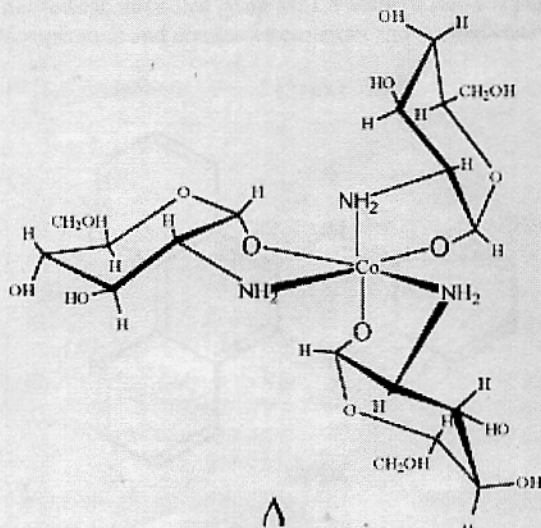
Mixed bis-phenanthroline Co(III) complexes with amino sugars disproportionate over a period of months, giving non-ionic tris-(aminosugar)complexes. The complex with  $\alpha$ -D-glucosamine has the  $\Lambda$ -configuration with facial isomerism on the base of molecular composition and absorption and circular dichroism spectra.

Mixed Co(III) complexes of bis-phenanthroline (phen) and an aminosugar ( $\alpha$ -D-glucosamine;  $\alpha$ -D-galactosamine or  $\beta$ -D-mannosamine) [1] disproportionate over a period of months into Co(III)(phen)<sub>3</sub>, Co(II)(H<sub>2</sub>O)<sub>6</sub> and Co(III)(aminosugar)<sub>3</sub> [2]. The isolation, characterization and stereochemistry of the D-glucosamine complex, Co(III)(D-glucosamine)<sub>3</sub>, is described.

The  $\Lambda$  mixed complex with  $\alpha$ -D-glucosamine was left, as an aqueous solution, for 2 months at room temperature, and the tris-D-glucosamine complex was isolated chromatographically on SP-Sephadex C25 by elution with NaCl in a gradient of concentrations, ranging from 0.02 to 0.1 M, and monitoring the optical activity of the fractions. The optically active fractions were concentrated to dryness and extracted with MeOH to remove NaCl. Both the tris-phenanthroline and hexa-aquo complexes are racemic in the conditions of the experiment [3].

Microanalysis for [Co( $\alpha$ -D-glucosamine)<sub>3</sub>]5H<sub>2</sub>O gave: Co 8.51 (8.64); C 31.0% (31.63); N 5.98% (6.15); H 6.52% (6.73). Calculated values are inside parenthesis.

The absorption and circular dichroism spectra (Figure and Table) are characteristic of the  $\Lambda$ -configuration at Co(III) [4] and the structure is shown in the following Scheme for the neutral complex:



Scheme

Generally the absorption and CD bands at ca. 550 nm, due to the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  transition are characteristic of low symmetry octahedral complexes with three bonded nitrogens and three oxygens [5]. In this case there are two CD signals of opposite signs. They can be related with the  ${}^1A_1$  and  ${}^1E_2$  states of Co(III) under  $C_3$  microsymmetry, with facial isomerism [5]. The absorption spectrum has a shoulder at ca. 400 nm, corresponding to a  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transition with a positive DC signal, as expected for this type of isomerism (Figure and Table) [4, 5].

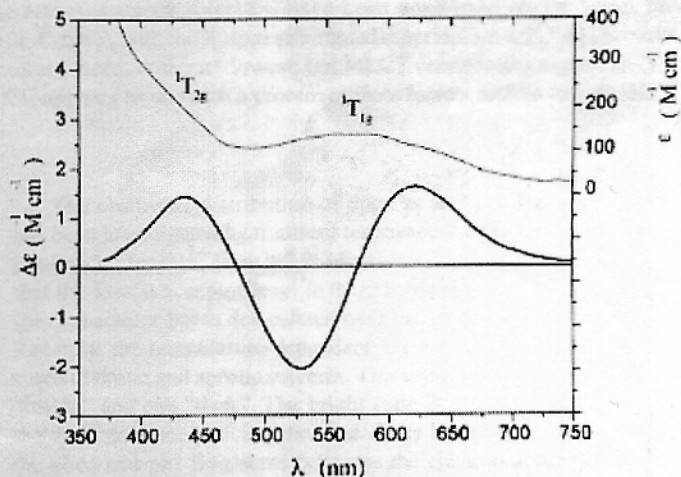


Fig.: Absorption and circular dichroism spectra in the visible region of the complex  $\Lambda$ -[Co(D-glucosamine)<sub>3</sub>]

Table: Values of absorption and circular dichroism for complexes  $\Lambda$ -[Co(D-glucosamine)<sub>3</sub>]

|               | $\lambda$ , nm | log $\epsilon$ | $\lambda$ , nm <sup>b</sup> | $\Delta\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> ) |
|---------------|----------------|----------------|-----------------------------|--|
| D-glucosamine | 420h           | 2.47           | 435                         | +1.4   |
|               | 568            | 2.13           | 529                         | -2.0   |
|               |                |                | 622                         | +1.6   |

Mixed Co(III) complexes of bis-phenanthroline and aminosugars involve cis-NH<sub>2</sub>-O<sup>-</sup> ligands, i.e., in the present complexes: equatorial NH<sub>2</sub> and axial, α-O<sup>-</sup> [1,2], as in Scheme.

On the basis of preliminary results, the configuration of the tris-α-D-galactosamine complex is similar to that of the complex with D-glucosamine. Characterization of this last compound will be covered in more detail elsewhere.

## REFERENCES

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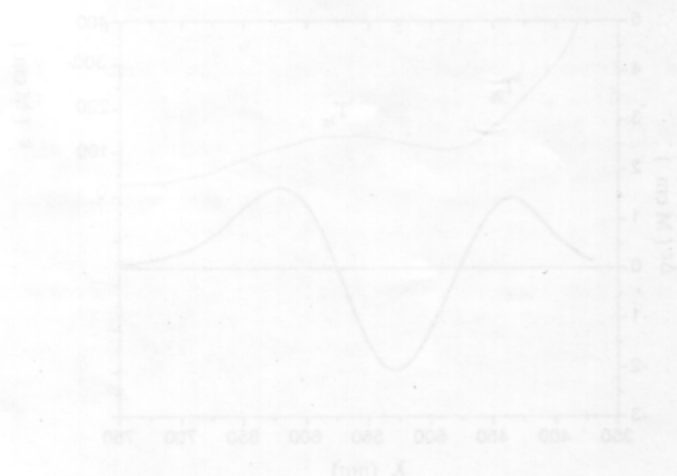


Fig. 1. Absorption and circular dichroism spectra in the visible region of the complex A [Co(III)-galactosamine].

Table. Values of absorption and circular dichroism for complex A [Co(III)-galactosamine].

| $\lambda$ , nm | $\log \epsilon$ | $\log \theta$ , deg cm <sup>2</sup> dmol <sup>-1</sup> |
|----------------|-----------------|--|
| 210            | 2.47            | +1.8   |
| 280            | 2.13            | -2.0   |
| 440            | 0.23            | +1.8   |

Mixed Co(III) complexes of bis-phenanthroline (phen) and α-D-galactosamine (α-D-gal) or α-D-glucosamine (α-D-glc) were prepared in a 1:1 molar ratio. The absorption and circular dichroism spectra of the complexes were recorded in the visible region (200-600 nm) and the results are shown in Table. The absorption spectra of the complexes show a maximum at 210 nm and a minimum at 280 nm. The circular dichroism spectra show a positive peak at 210 nm, a negative peak at 280 nm, and a smaller positive peak at 440 nm. The results are similar to those reported for the corresponding α-D-glucosamine complexes.

Microanalysis for [Co(III)-galactosamine] (10.00): Calcd. C, 31.04; H, 5.38; N, 12.57; O, 49.01. Found: C, 31.02; H, 5.35; N, 12.55; O, 49.00.

The absorption and circular dichroism spectra (Fig. 1 and Table) of the complex of the A configuration of Co(III) and the sugar is shown in the following Scheme for the neutral complex.

