STEREOSELECTIVE SYNTHESIS OF TRIS[DI-M-HYDROXY-BIS-(ETHYLENEDIAMINE)] TETRACOBALT(III)

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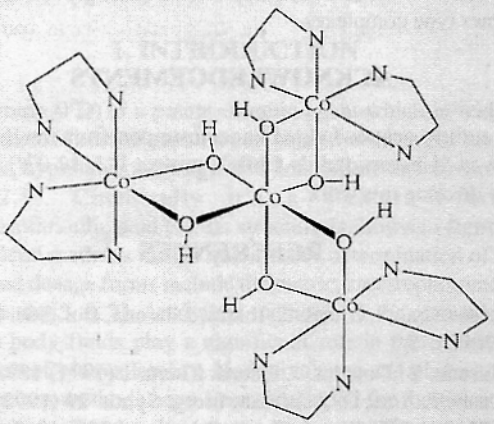
ABSTRACT

Tetranuclear complexes of Co(III) with bidentate ligands and hydroxo bridges were synthesized in the presence of D-glucosamine, D-mannosamine, D- and L-xylose with the partial resolution the these complexes.

INTRODUCTION

In a previus publication [1] we showed that aminosugars and pentoses induce stereoselective synthesis of the "Werner complex", also known as "hexol". We have now extended the work by synthesizing tetranuclear Co(III) complexes, the so-called "Werner type complexes", $[Co_4(OH)_6(C_2N_2H_8)_6]^{6+}$, where the NH_3 ligands of the original Werner complex are replaced by ethylenediamine (en) (Fig.1), with the aim of studying the effect of this ligand on the stereoselectivity in this reaction.



Δ

Fig. 1. Structure of Δ-$[Co_4(OH)_6(C_2N_2H_8)_6]^{6+}$.

EXPERIMENTAL

A solution of 9.2 g of cobalt(II) nitrate hexahydrate (0.05 moles) in 7 mL of water was mixed with 12 mL of ethylenediamine in the presence of 0,01 moles of carbohydrate. The solution was stirred for about 30 minutes, to oxidize Co(II) to Co(III), as its colour changed from pink to dark red. The solution was then filtered to remove any residue of cobalt oxide, and was then left at room temperature.

After 48 hours the first brown crystals appeared. They were washed with ethanol, 95%, and left in a desiccator with calcium chloride for 48 hours. The elemental analysis is in Table 1. The absorption spectra were obtained in a Unicam UV3 spectrometer (Table 2) and the circular dichroism (C.D.) spectra were obtained in a Jobin-Ivon CD 6 model dichrograph (Fig. 3). The cobalt content of the complexes was determined by atomic absorption in a Perkin Elmer Model 3110 spectrometer and the elemental analysis was made in a Fisons-Carlo Erba EA 1108 analyzer.

Table 1. Elemental analyses of $[Co_4(OH)_6(C_2N_2H_8)_6](NO_3)_6 \cdot 6H_2O$, synthesized in the presence of the carbohydrate.

	%N	%C	%H	%Co
D-glucosamine	20.69	12.52	5.98	20.08
D-mannosamine	20.94	12.74	6.00	20.09
D-xylose	21.03	12.74	6.00	20.08
L-xylose	20.97	12.88	5.96	20.55
Calculated	21.41	12.23	5.78	20.02

Table 2. Extinction coefficients of $[Co_4(OH)_6(C_2N_2H_8)_6](NO_3)_6 \cdot 6H_2O$.

λ, nm	logε
492	0.62
615	0.55

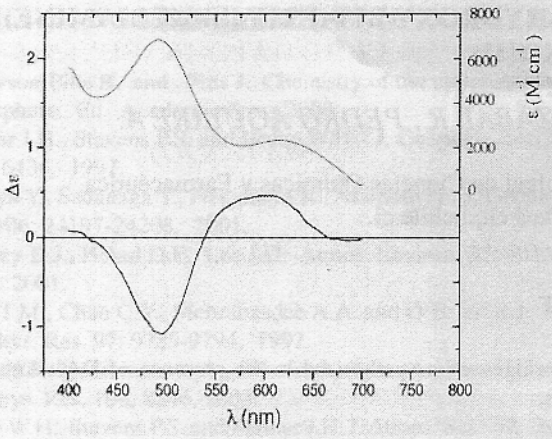


Fig. 3. Absorption and circular dichroism spectra of $[Co_4(OH)_6(C_2N_2H_8)_6]^{6+}$ synthesized in the presence of the D-xylose.

The circular dichroism spectra were obtained on of 20 mg of sample in 10 mL water; and to absorption spectra with 5 mg complex in 10 mL water.

Stereoselectivity was induced by: D-glucosamine, D-mannosamine, D- and L-xylose. Results were unsatisfactory with D-glucose, judging from the C.D. and absorption spectra.

RESULTS AND DISCUSSION

The absorption spectra of the synthesized complexes in the presence of the different carbohydrates showed two bands, one at 615 nm, assigned to the electronic transition corresponding to the $^1T_{1g}$ state of the chromophoric $Co(III)O_6$ group and the other at 491 nm corresponding to the $^1T_{1g}$ state of the three chromophoric $Co(III)N_4O_2$ groups (Fig. 3).

The circular dichroism spectra (Fig 3) show two signals of opposing sign, one at 682 nm and the other at 610 nm, the intensity and sign sequence depending on the carbohydrate used in the synthesis. At 492 nm, there is a signal corresponding to the second absorption band, followed by a very weak signal of opposite sign at 380 nm. From the circular dichroism intensity of the totally resolved complex [2], we estimated the percentage resolution induced by each carbohydrate (Table 3).

The degree of resolution for this complex is lower than that observed for the Werner complex, but the absorption spectra for both complexes are very similar, as expected for the identical chromophoric groups in both types of compounds: $Co(III)O_6$ and $Co(III)N_2O_4$ [3] (Fig.2).

The circular dichroism signal at approximately 500 nm, corresponding to the $^1A_1 \rightarrow {}^1T_1$ component of the $Co(III)N_4O_2$ chromophore [2], is very similar for hexol and the ethylenediamine complex, showing that replacement of the NH_3 ligands by ethylenediamine does not affect this electronic transition.

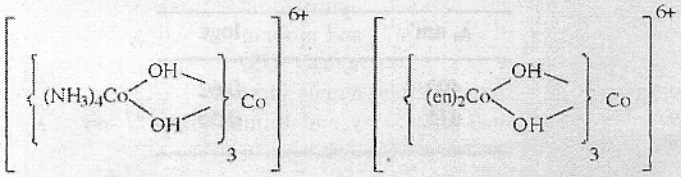


Fig. 2. Chromophoric groups $Co(III)N_4O_2$ and $Co(III)O_6$.

In a previous publication [1] we concluded that the stereoselective effect of the carbohydrates involves preferred hydrogen bonding between the carbohydrate OH groups and the bridging OH groups, with one of the isomers. It seems that the ethylenediamine rings in the present complexes sterically disfavor this interaction consistent with the lower stereoselectivity induced by the carbohydrates in this rather than in the Werner complex. For the D-carbohydrates examined the predominant Werner or Werner type complex is Δ, although the extents of stereoselectivity are significantly lower with the latter (Table 3).

Table 3. Effect of the carbohydrate on the predominant isomer and percentage resolution in Werner type ethylenediamine complexes.[a]

	Predominant Isomer	% Resolution
D-glucosamine	Δ	12.7 (15.9)
D-mannosamine	Δ	3.1 (5.6)
D-xylose	Δ	2.5 (4.3)
L-xylose	Λ	2.3 (4.1)

[a] Data on the Werner complex are in parentheses, ref. [1].

The absolute configuration at $Co(III)O_6$ is based on the circular dichroism spectrum as described by Mason and Wood in terms of the sign sequence of the signals of the major C.D. band [4].

The visible circular dichroism signals of these complexes are much stronger than for the d → d transitions of mononuclear tris-chelate Co(III) complexes [4] probably due to interactions between the absorption bands of the two chromophoric Co(III) groups in the Werner and Werner type complexes.

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