

COMPLEXATION OF MANNOSAMINE WITH COBALT(III) BIS-PHENANTHROLINE. ISOLATION OF A STABLE TRIIODIDE SALT

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ABSTRACT

D- β -Mannosamine reacts with cobalt(III) bis-phenanthroline to form a single 1:1 complex with the Δ configuration at Co(III) which can be isolated as the stable triiodide salt.

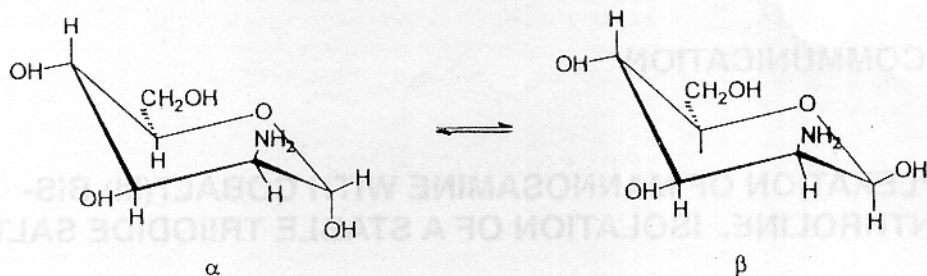
RESUMEN

La D- β -Manosamina reacciona con cobalto(III) bis-fenantrolina para formar un sólo compuesto en que la razón entre los reaccionantes es 1:1. El complejo resultante tiene la configuración Δ en torno al Co(III) y se puede aislar como triyoduro, constituyendo la sal un producto estable.

Complexes of sugar and other polyols with metal ions are well studied¹⁻³⁾ and binding of bidentate ligands preferentially involves 1,2-cis (ax,eq) groups⁴⁾. We have examined mixed complexes of cobalt(III) with ammonia or diamines and keto- or amino-sugars. 1,10-phenanthroline(phen) is a useful ligand because its ¹H-NMR signals are well separated from those of the sugars and it is planar, which simplifies molecular modeling. Configuration at Co(III) is assigned from the circular dichroism (CD) or optical rotatory dispersion (ORD) spectra⁵⁾. These complexes are reasonably stable in solution, but, as solids, with e.g. SO₄²⁻, as counterion, they partially decompose within a few days which creates a major problem in the study of these and similar Co(III) complexes⁶⁾. We found that stable solid complexes can be isolated with I₃⁻ as counterion.

The bis(phenanthroline) complex of Co(III) with D-glucosamine(2-amino-2-deoxy-D-glucopyranose) is a Δ - and Λ -mixture and $\Delta/\Lambda = 16$ ^{6a)}. Complexation is with the α -anomer and involves eq-NH₂ and ax-1-OH^{6b)}. D-Mannosamine(2-amino-2-deoxy-D-mannopyranose) is an α - and β -mixture in the ¹C₁ conformation. The preferred antiaxial orientation of 1-OH and 2-NH₂ in the α -anomer (Scheme 1) disfavors complexation as compared with the β -anomer with eq-1-OH and ax-2-NH₂, but the configuration at Co(III) has to be determined.

The complex was prepared from [Co(phen)₂Cl₂]Cl and D-mannosamine as described for D-glucosamine^{6a)}. One optically active complex, with the Δ -configuration, was isolated chromatographically (Sephadex C-25 K⁺ form). The tricationic salt precipitates from H₂O on addition of KI₃, but it is sparingly soluble in methanol and readily soluble in acetone and acetonitrile.



SCHEME 1

The complex was isolated as $[\text{Co}(\text{phen})_2\text{-D-mannosamine}](\text{I}_3)_3$; Calc: C, 20.70; H, 1.67; N, 4.00; Co, 3.37%. Found: C, 20.90; H, 2.14; N, 4.0; Co, 3.54%. The $^1\text{H-NMR}$ spectrum (500 MHz) was assigned by homonuclear decoupling and $^1\text{H-COSY}$: H-1, 4.13d; H-2, 3.64m; H-3, 3.87dd; H-4, 3.98 ψ t (pseudo triplet); H-5, 3.04 m; H-6, 3.68dd; H-6', 3.57dd, referred to acetone at 2.05 ppm. J_{12} 1.5; J_{23} 5.0; J_{34} 9.5; J_{45} 9.5; J_{46} 9.0; J_{56} 5; $J_{56'}$ 2.5; $J_{66'}$ 12 Hz. The CD spectra were monitored on a Jobin-Ivon DC6 spectrometer. Absorbance (λ and ϵ) and CD (λ and $\Delta\epsilon$) spectra of the chloride in water are shown in Table I, and are similar to those of the corresponding Δ -complex with D-glucosamine^{6a)}. These complexes are dicationic in water at pH > 7 due to deprotonation of the 1-OH group complexes to $\text{Co}(\text{III})$ ^{2,3)}. The structure, modeled as described with MM2 parameters²⁾ is predicted to be more stable than those of the Λ -complex or with the α -anomer (Fig. 1).

TABLE I. Electronic absorbance ($\text{mol}^{-1}\text{M}^{-1}$) and circular dichroism spectra^a ($\text{cm}^{-1}\text{M}^{-1}$).

λ max (nm)	log ϵ	λ (nm)	$\Delta\epsilon$
		223	-7.8
		235	+20.0
272 ^b	4.72	268	+67.0
300(sh)	4.27	281	-78.0
320(sh)	3.90	316	+12.0
391(sh)	2.49	389	+1.02
491	2.23	501	-3.0

^aAqueous solution after chromatography and analysis of $\text{Co}(\text{III})$, similar CD signals were obtained with a solution of the I_3^- salt in acetone in spectrally accessible UV regions;

^bThere is strong absorbance at lower wavelengths.

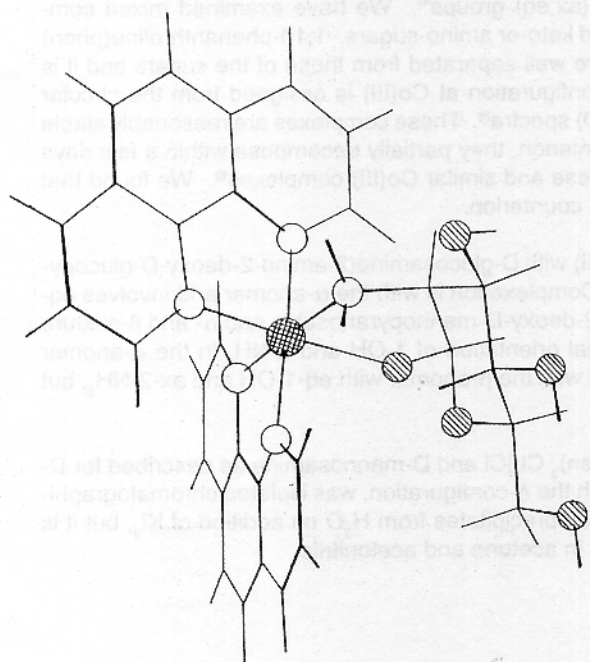


FIG. 1. Predicted structure of dicationic Δ - $\text{Co}(\text{III})(\text{phen})_2\text{-}\beta\text{-D-mannosamine}$. Hydrogens are shown as sticks; Cobalt, O; Nitrogen, O; Oxygen, O.

The use of I_3^- , a weak oxidant, apparently stabilizes the solid complex, probably by inhibiting formation of $Co(II)$ species. We also used this procedure to isolate the Δ - and Λ -complexes of $Co(III)(phen)_2$ with D-galactosamine. These solid complexes retained their analytical composition and absorbance and CD spectra over two months and I_3^- appears to be a useful counterion for the isolation of $Co(III)$ complexes.

ACKNOWLEDGEMENTS

Support of this work by FONDECYT and the Fundación Andes is gratefully acknowledged. Upgrading of the 500 MHz NMR spectrometer was made possible by National Science Foundation Grant CHE-9407775.

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