Complexes of Co(III) with L-sorbose and phenanthroline

Andrei Blaskó [a], Clifford A. Bunton [a,*], Exequiel Moraga [b],
Sergio Bunel [b,*], Carmen Ibarra [b]

[a] *Department of Chemistry, University of California, Santa Barbara, CA 93106, USA*
[b] *Departamento de Química Inorgánica y Analítica, Facultad de Ciencias Químicas y Farmacéuticas,
Universidad de Chile, Santiago, Casilla 233, Chile*

Abstract

L-Sorbose and two molecules of 1,10-phenanthroline form a complex with Co(III) which has
the Λ configuration about Co(III), based on CD and ORD spectra. The ^{1}H NMR signals of
α-L-sorbopyranose and its mixed Co(III)(phen)$_2$ complex have been assigned. Signals of H-6 and
H-6' of the sugar are shifted strongly upfield because of shielding by the aromatic residues, but
shifts are much smaller for H-1 and H-1'. These observations are consistent with molecular
modelling with MM2 parameters, which predicts that the most stable complex is the Λ
diastereomer with complexation at positions 1 and 2. The characteristics of the NMR spectra and
the predicted structure of the complex differ from those of the corresponding complex of
D-fructose.

Keywords: Cobalt; L-Sorbose; Phenanthroline; Complexes

1. Introduction

Sugars and their derivatives can form complexes with metal ions and behave as bi- or
tri-dentate ligands [1–4]. The structural factors that control stabilities are well estab-

Table 1
Electronic absorbance and circular dichroism spectra of the Λ-complex

Absorbance [a]		CD	
λ_{max} (nm)	log ϵ	λ (nm)	$\Delta\epsilon$
515	2.23	510	+ 5.5
		400	− 3.4
		360	+ 1.6
(295)	(3.63)	317	− 11
274	4.02	280	+ 47
< 230		267 [b]	− 48
		241 [b]	− 43
		226 [b]	84
		(210) [b]	

[a] Values in parentheses are for shoulders. Units of ϵ and $\Delta\epsilon$ are cm^{-1} mol^{-1} L.
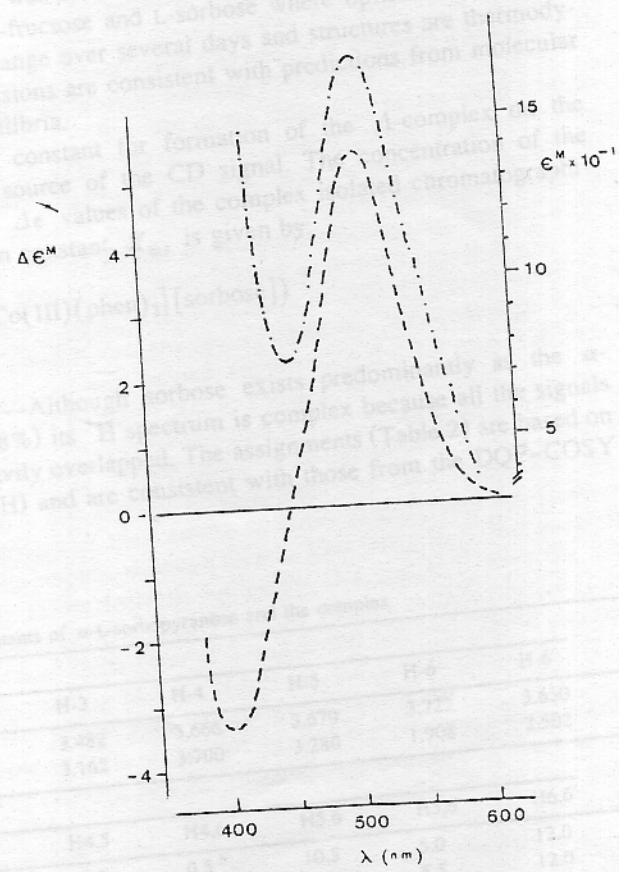[b] Complex was chromatographed but not isolated as a solid.

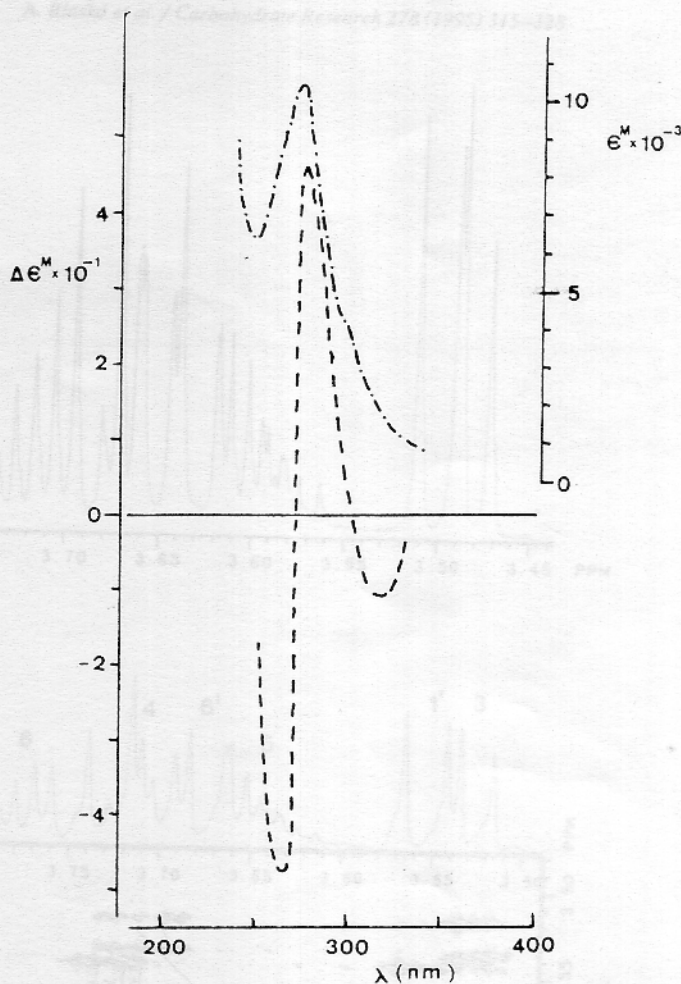Fig. 1. Absorbance and CD spectra in the visible region. Absorbance (- · -), CD (—).

Fig. 2. Absorbance and CD spectra in the UV region. Key as in Fig. 1.

The sign sequence indicates that the chiral species has the Λ-configuration [6]. The CD spectrum obtained after chromatographic separation, but without isolation of the solid complex, agrees with that of the crystalline complex separated chromatographically, although because of improved instrumentation we saw additional CD signals in the UV region (Experimental). These signals are shown in Table 1. Examination of the ORD visible spectrum (data not shown) confirms this assignment.

The Λ-configuration at Co(III) is preferred in complexes of both D-fructose [5] and L-sorbose with Co(III)(phen)$_2$. The different behaviors of the mixed complexes of Co(III)(en)$_2$ with fructose and sorbose, where the Δ-configuration is preferred with the fructose complex and the Λ-with the sorbose complex [12], may be related to the relative flexibility of the aliphatic diamine as compared to the rigidity of phenanthroline.

Complexes of Co(III) with sugar derivatives that have the same configuration at the metal have similar CD and absorbance spectra in the UV and visible regions with slight shifts due to the numbers of oxygen and nitrogen atoms coordinated to the octahedral center [4,5,15].

The absorbance and CD spectra of these ketose complexes are very similar to those of the corresponding complexes of D-glucosamine with $Co(III)(phen)_2$, apart from a slight red shift due to differences in the numbers of nitrogen and oxygen atoms coordinated to Co(III). Assignments of the absorbance bands and CD signals are essentially the same as those given for Co(III) glucosamine complexes [4], and for other metal complexes with ligands of biological interest [14].

We saw only one Λ-complex of L-sorbose and $Co(III)(phen)_2$ although D-fructose gives largely Λ- with smaller amounts of a Δ-complex [5]. In some systems, e.g., in the formation of complexes of $Co(III)(phen)_2$ with amino acids and related compounds, exclusive formation of one complex was ascribed to kinetic control [16]. The situation is different for the complexes with D-fructose and L-sorbose where optical rotations and NMR spectra in solution do not change over several days and structures are thermodynamically controlled. These conclusions are consistent with predictions from molecular modelling which are based on equilibria.

We estimated the equilibrium constant for formation of the Λ-complex on the assumption that it was the sole source of the CD signal. The concentration of the complex was calculated by using $\Delta\epsilon$ values of the complex isolated chromatographically (Table 1) and the association constant, K_{ass} is given by:

$$K_{ass} = [\Lambda - complex] / ([Co(III)(phen)_2][sorbose])$$

and $K_{ass} = 11 \ M^{-1}$.

NMR spectra of L-sorbose.—Although sorbose exists predominantly as the α-pyranose tautomer [9,10] (96–98%) its ^1H spectrum is complex because all the signals are within 0.24 ppm and are heavily overlapped. The assignments (Table 2) are based on the HETCOR spectrum ($^{13}C-^1H$) and are consistent with those from the DQF–COSY

Table 2
^1H Chemical shifts and coupling constants of α-L-sorbopyranose and the complex

	δ [a] (ppm)						
	H-1	H-1'	H-3	H-4	H-5	H-6	H-6'
Sorbose	3.684	3.500	3.482	3.666	3.670	3.722	3.650
Complex	3.683	2.882	3.162	3.700	3.280	1.908	2.502

	J (Hz)						
	H-1,1'	H3,4	H4,5	H4,6	H5,6	H5,6'	H6,6'
Sorbose	11.5	9.5	10.0	0.5 [b]	10.5	5.0	12.0
Complex	11.5	10.0	10.5		8.5	5.5	12.0

[a] In D_2O at 25°C relative to sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS).
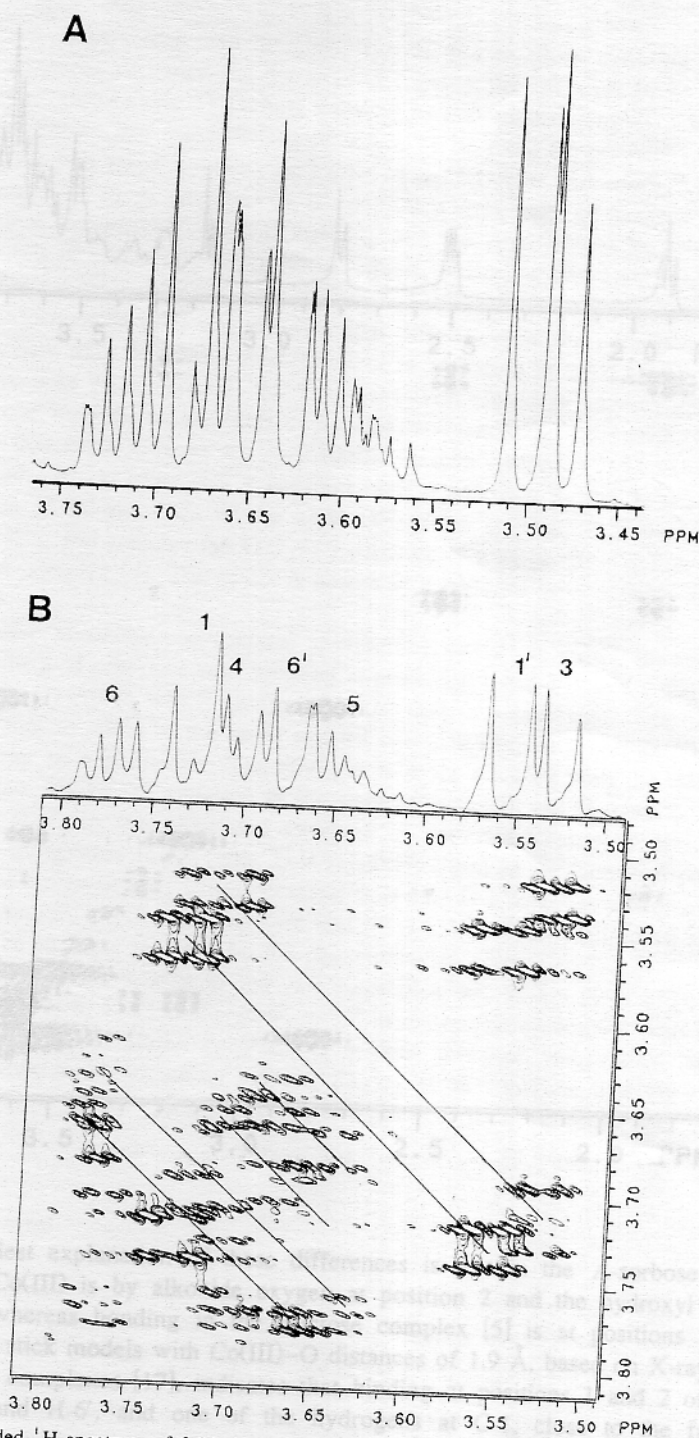[b] Long-range coupling.

Fig. 3. (A) Expanded ^{1}H spectrum of 0.01 M L-sorbose in D$_2$O at 25°C. (B) DQF–COSY ^{1}H spectrum of 0.01 M L-sorbose in D$_2$O at 25°C.

Table 3
Changes in ^{1}H chemical shifts on formation of Λ-complexes of fructose and sorbose [a]

	H-1	H-1'	H-3	H-4	H-5	H-6	H-6'
Sorbose	0.0	−0.62	−0.32	0.03	−0.39	−1.81	−1.15
Fructose	−1.21	−1.33	0.04	−0.42	−0.46	−0.38	−0.87

[a] Values of $\Delta\delta$, ppm from data in Table 2 and ref. [5], relative to chemical shifts of the sugars.

spectrum (Fig. 3). Our ^{13}C chemical shifts (Experimental) agree with literature values [10] with minor differences due to our using a relatively low sugar concentration (0.1 M). We neglect the ^{1}H signals of the minor furanose tautomer [10].

The coupling constants of the α-pyranose tautomer (Table 2) are consistent with axial hydrogens at positions 3, 4, 5, and 6, and the equatorial H-6' has a lower chemical shift than H-6. There is long-range coupling between H-4 and H-6, consistent with their diaxial periplanar relation. This long-range coupling was not seen with β-D-fructo-pyranose [5,7] possibly because the pseudo-axial OH group at position 5 causes slight ring flattening and limits a periplanar relation between H-4 and H-6.

NMR spectra of sorbose complex.—Because of the instability of the solid complex and formation of Co(II) species we examined only the complex formed in situ [5]. There is interference with signals of uncomplexed sorbose because the complex does not form quantitatively (Experimental). Some of the ^{1}H signals of complexed sorbose are to the right of those of the sugar and the ^{1}H signals of the phenanthroline ligands are well to the left. They do not interfere with other signals [5] and were not examined.

There are strong ^{1}H signals with $\delta < 3.5$ ppm (relative to DSS) (Table 2) which must be those of a complex and some hydrogens are shielded by phenanthroline ligands. There are also some very small, but well defined, signals with $\delta < 3.5$ ppm. They are at 2.13 (t) and 3.00 (d) ppm and are probably due to a minor complex.

The DQF–COSY spectrum of the sorbose complex is very different from those of the fructose complexes [5], especially as regards locations of signals of H-1, H-1', H-6, and H-6' (Fig. 4). Signals of H-1 and H-1' in these ketoses and their complexes can be assigned unambiguously because of their strong geminal coupling and the absence of strong coupling with other hydrogens, although there is long range H-1'–H-3 coupling in the fructose complexes [5]. In the fructose complexes H-1 and H-1' have the lowest chemical shifts, but the situation is very different in the sorbose complex where H-6 and H-6' have the lowest chemical shifts (Tables 2 and 3 and ref. [5]). These signals are assigned by their geminal coupling and for H-6,6' by the vicinal coupling with H-5. Assignments of H-4 and H-3 follow from the 2D spectrum (Fig. 4).

Comparison of the chemical shifts of the sorbose and fructose complexes, relative to those of the parent sugars (Tables 2 and 3), indicates that the Λ-complexes have very different structures. In the Λ-sorbose complex the strong shifts of the H-6 and H-6' signals to the right are evidence for these hydrogens being close to the face of a phenanthroline ring, and the H-1 and H-1' signals are less strongly affected by complexation. In the Λ-fructose complex, upfield shifts were larger with H-1 and H-1' than with H-6 and H-6' because of differing interactions with the phenanthroline ligands [5].
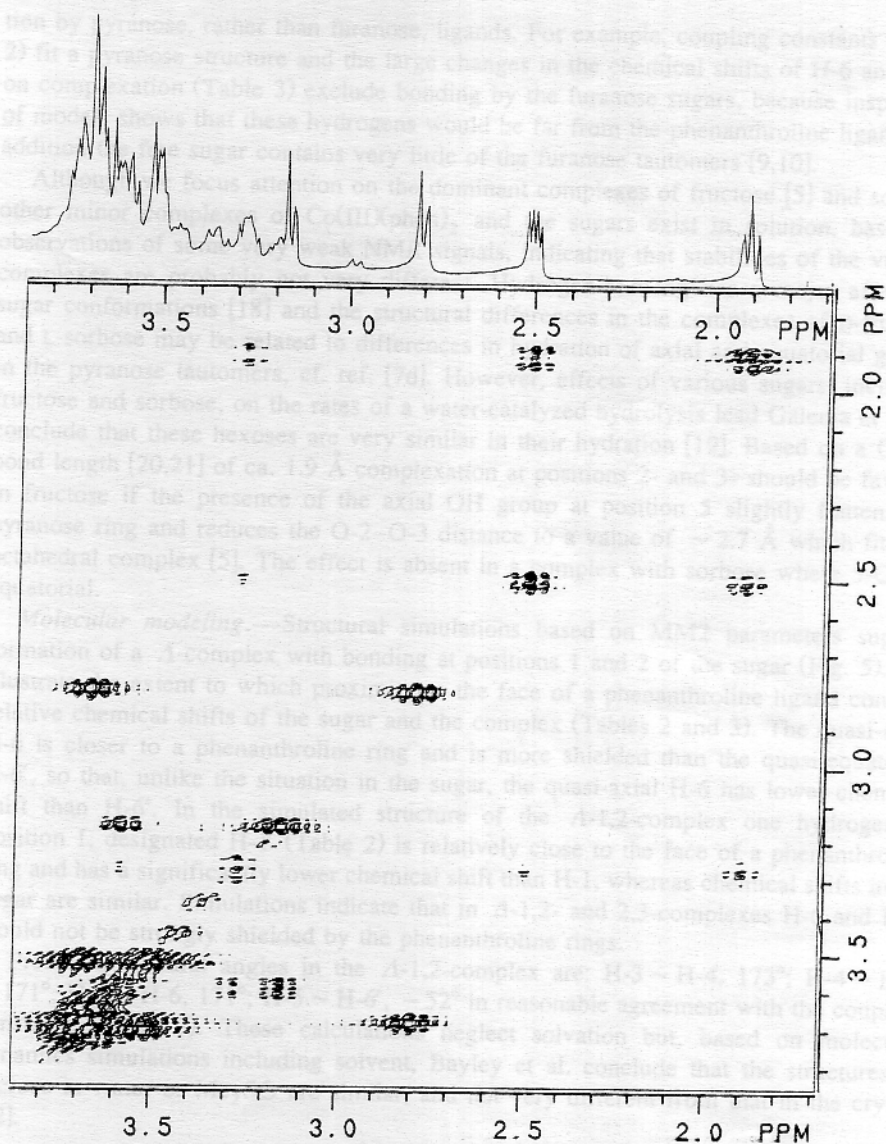
The simplest explanation of these differences is that in the Λ-sorbose complex bonding to Co(III) is by alkoxide oxygen at position 2 and the hydroxyl group at position 1, whereas bonding in the fructose complex [5] is at positions 2 and 3. Inspection of stick models with Co(III)–O distances of 1.9 Å, based on X-ray data on other Co(III) complexes [17], indicates that binding at positions 1 and 2 of sorbose brings H-6 and H-6', and one of the hydrogens at C-1, close to the face of a
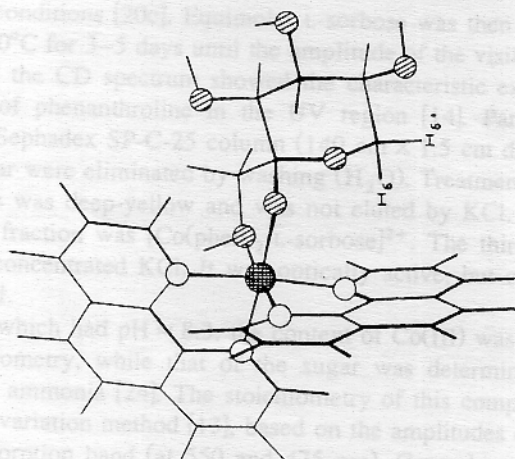
Fig. 5. Simulated structure of the Λ-complex of Co(III)(phen)$_2$ with α-L-sorbopyranose with complexation at oxygens at positions 1 and 2. Hydrogens are indicated by sticks. ● cobalt; ○ nitrogen; ◉ oxygen.

phenanthroline ring so that strong shielding decreases the chemical shifts. If bonding involves position 1 this shielding will be partially offset by electron withdrawal by Co(III). We used molecular modelling based on MM2 parameters to test this hypothesis (Fig. 5).

The strong coupling between axial hydrogens at positions 3, 4, and 5, and 4 and 6 in α-L-sorbopyranose (Table 2) indicates that these hydrogens are antiperiplanar. The situation is slightly different for the complex where distortion of the pyranose ring eliminates the long-range coupling between H-4 and H-6.

Sorbose and fructose as bidentate ligands.—The striking differences in the ^{1}H NMR spectra of the complexes of α-L-sorbose and β-D-fructose with Co(III)(phen)$_2$ show that, despite structural similarities in the sugars, complexation involves different hydroxyl groups. It is highly probable that binding involves alkoxide oxygen at position 2, because of the acidity of anomeric OH groups [17]. Therefore if complexation of sorbopyranose to Co(III) involves oxygens at positions 1 and 2, complexation of β-D-fructopyranose is at positions 2 and 3, consistent with earlier conclusions [5]. Complexation of hydroxy groups at the other positions is geometrically unfavorable. We did not see long-range coupling between hydrogens at positions 1 and 3 of the sorbose complex (Table 2), although it was observed with the fructose complex [5]. This result is consistent with predictions of molecular modelling which places H-1 periplanar to H-3 in the fructose [5], but not in the sorbose, complex.

Despite structural differences the preferred configuration at Co(III) is Λ in both the sorbose and fructose complexes. With fructose Λ- and Δ-complexes coexist, although the former predominates [5], but with sorbose very little, or no, Δ-complex is formed and molecular modeling indicates that this configuration is disfavored in either 1,2- or 2,3-complexes.

Our NMR evidence on the complexes of both sorbose and fructose [5] fits complexa-

tion by pyranose, rather than furanose, ligands. For example, coupling constants (Table 2) fit a pyranose structure and the large changes in the chemical shifts of H-6 and H-6' on complexation (Table 3) exclude bonding by the furanose sugars, because inspection of models shows that these hydrogens would be far from the phenanthroline ligands. In addition the free sugar contains very little of the furanose tautomers [9,10].

Although we focus attention on the dominant complexes of fructose [5] and sorbose other minor complexes of Co(III)(phen)$_2$ and the sugars exist in solution, based on observations of some very weak NMR signals, indicating that stabilities of the various complexes are probably not very different. Hydrogen-bonding has a major effect on sugar conformations [18] and the structural differences in the complexes of D-fructose and L-sorbose may be related to differences in hydration of axial and equatorial groups in the pyranose tautomers, cf. ref. [7d]. However, effects of various sugars, including fructose and sorbose, on the rates of a water-catalyzed hydrolysis lead Galema et al. to conclude that these hexoses are very similar in their hydration [19]. Based on a Co–O bond length [20,21] of ca. 1.9 Å complexation at positions 2- and 3- should be favored in fructose if the presence of the axial OH group at position 5 slightly flattens the pyranose ring and reduces the O-2–O-3 distance to a value of ∼ 2.7 Å which fits the octahedral complex [5]. The effect is absent in a complex with sorbose where 5-OH is equatorial.

Molecular modeling.—Structural simulations based on MM2 parameters support formation of a Λ-complex with bonding at positions 1 and 2 of the sugar (Fig. 5), and illustrate the extent to which proximity to the face of a phenanthroline ligand controls relative chemical shifts of the sugar and the complex (Tables 2 and 3). The quasi-axial H-6 is closer to a phenanthroline ring and is more shielded than the quasi-equatorial H-6', so that, unlike the situation in the sugar, the quasi-axial H-6 has lower chemical shift than H-6'. In the simulated structure of the Λ-1,2-complex one hydrogen at position 1, designated H-1' (Table 2) is relatively close to the face of a phenanthroline ring and has a significantly lower chemical shift than H-1, whereas chemical shifts in the sugar are similar. Simulations indicate that in Δ-1,2- and 2,3-complexes H-6 and H-6' would not be strongly shielded by the phenanthroline rings.

Predicted dihedral angles in the Λ-1,2-complex are: H-3 ∼ H-4, 173°; H-4 ∼ H-5, −171°; H-5 ∼ H-6, 171°; H-5 ∼ H-6', −52° in reasonable agreement with the coupling constants (Table 2). These calculations neglect solvation but, based on molecular dynamics simulations including solvent, Bayley et al. conclude that the structures of sucrose in water or Me$_2$SO are similar, and not very different from that in the crystal [22].

3. Experimental

Complex formation.—The mixed complex of phen and sorbose with Co(III) was prepared by the procedure used with the corresponding complexes of fructose [5]. An aqueous 0.025 M solution (25 mL) of *cis*-[Co(phen)$_2$Cl$_2$]Cl [23] at pH 7–8, adjusted with NaOH, was allowed to aquate to the *cis*-diaquo complex with a color change from violet to red. The diaquo complex, [Co(phen)$_2$(OH$_2$)$_2$]$^{3+}$ should be deprotonated under

the preparative conditions [20c]. Equimolar L-sorbose was then added and the solution was kept at ~ 20°C for 3–5 days until the amplitude of the visible ORD signal reached a maximum and the CD spectrum showed the characteristic excitonic splitting of the $\pi \rightarrow \pi^*$ bond of phenanthroline in the UV region [14]. Part of this solution was transferred to a Sephadex SP-C-25 column (140 cm × 1.5 cm diameter, K^+ form) and salt and free sugar were eliminated by washing (H_2O). Treatment with 0.1 M KCl gave three bands. One was deep-yellow and was not eluted by KCl. The second, deep-red, optically active, fraction was $[Co(phen)_2$-L-sorbose$]^{2+}$. The third, pale-pink band was eluted by more concentrated KCl. It was optically active, but contained no sugar and rapidly racemized.

In fraction 2, which had pH ≈ 8.3, the content of Co(III) was determined by atomic absorption spectrometry, while that of the sugar was determined by oxidation with Ce(IV) sulfate in ammonia [24]. The stoichiometry of this complex was confirmed by Job's continuous variation method [13], based on the amplitudes of the Cotton effect of the first d–d absorption band (at 550 and 475 nm). Control experiments showed that phenanthroline was not displaced from Co(III) by the sugar. Absorbance and CD spectra of this fraction were measured after dilution.

The high solubility of the chloride salt of the mixed complex prevented its crystallization, so the sulfate was isolated. The chloride salt was prepared at pH 8 and after reaction the solution was transferred to a column of Dowex 1 × 4 (sulfate form). The solution of the sulfate salt after concentration in vacuo gave a microcrystalline red solid which was kept in vacuo over $CaCl_2$. It analyzed as $[Co(phen)_2$-L-sorbose$]_2(SO_4)_3 \cdot 2H_2O$: C, 46.80 (47.40); H, 4.50 (3.80); N, 7.40 (7.40); Co, 7.73 (7.78); S, 6.56 (6.63) {theoretical values in parentheses}. As with the corresponding fructose complex [5] the cationic charge differs in the crystal and in solution at pH 8, on the assumption that sulfate is the counterion. However, coordination of the 2-OH group to Co(III) may make it sufficiently acidic to protonate SO_4^{2-}, so that the structure could be that of a mixed sulfate–hydrogen sulfate [20c]. Analyses of C, H, and N were made on a PE 240-C analyzer. The concentration of Co(III) was determined on a PE 460-C or 305 atomic absorption spectrometer or by iodometric titration [25]. Analyses of SO_4^{2-} were made gravimetrically or by using a LECO IR sulfometer.

The time required for observation of maximum absorbance varied from one experiment to another, probably because of minor variations in the pH of the unbuffered reaction solutions. The rate of replacement of water and OH^- at Co(III) by the sugar should be pH dependent. The solid complex decomposed within a few days at room temperature, giving Co(II), but, as with the fructose complexes [5], solutions were more stable. The CD spectrum of the solutions did not change within one month or the ^1H NMR spectrum within 10 days.

Spectrometry.—The UV–vis absorbance spectra were monitored in Zeiss PMQ-2 or Cary-11 spectrophotometers. The CD spectra were generally monitored in a Cary 60 spectrophotometer and it, or a PE polarimeter with an attached monochromator, was used for the ORD spectra. Concentrations were as described for the fructose complex [5]. A sample of the complex was isolated chromatographically and its CD spectrum was measured on a Jobin-Yvon DC6 spectrometer and CD signals at $\lambda > 260$ nm (Table 1) were monitored on this instrument. CD spectra of a mixture of 0.01 M Co(III)(phen)$_2$

and 0.02 M sorbose (pH 8) were also monitored on a Jobin-Yvon DC6 spectrometer without isolation. The wavelengths of the CD signals in the visible region are similar to those obtained after isolation (Table 1), namely, 519 nm (positive), 402 nm (negative) and 356 nm (positive). The CD signals increased slightly between 1 and 3 days after mixing and from the CD signal at 519 nm and $\Delta\epsilon$ (Table 1) we calculate $K_{ass} = 11$ M^{-1}. We also estimated the equilibrium constant for complex formation from the optical activity of a chromatographed sample measured by using the PE polarimeter and this value was in reasonable agreement with that estimated from the CD spectrum. The CD signals are broad and the positions of the indicated maxima varied slightly from one experiment to the next.

NMR spectroscopy.—The ^{1}H NMR spectra (500 MHz, ^{1}H) were measured at 25°C on a GN-500 spectrometer in D_2O, as described for the fructose complex [5] in 16K data points with a spectral width of 799.36 Hz. Samples were prepared in situ from equimolar reactants at pD ≈ 8.4 and were left for ~ 2 days at 25°C, with concentration 0.01–0.2 M. The solutions contained unreacted sorbose and conditions involved a compromise between signal strength and line width which depended on electrolyte concentration. There was no interference from signals of the phenanthroline ligand. Phase-sensitive double quantum filtered COSY (DQF–COSY) [26] spectra were recorded as described [5] in 4K data points and 256 blocks. The ^{1}H chemical shifts and coupling constants were measured with expanded spectra. Chemical shifts of ^{1}H and ^{13}C were referred to sodium 4,4-dimethyl-4-silapentan-1-sulfonate (DSS). The ^{13}C (with and without ^{1}H decoupling) and the ^{13}C–^{1}H (HETCOR) spectra were recorded on the GN-500 spectrometer in 4K data points and 64 blocks. The ^{13}C chemical shifts of α-L-sorbopyranose at positions 1, 2, 3, 4, 5, and 6 are: 63.81; 97.93; 70.64; 74.05; 69.90, and 62.05 respectively (cf. ref. [10]). In the ^{1}H coupled spectra signals of C-1, C-4 and C-5 are doublets and that of C-2 is a singlet, consistent with the assignments [10]. The complex formed in situ had ^{13}C chemical shifts, relative to external Me_4Si, at 58.18 ppm, 69.81 ppm, 70.06 ppm, 74.36 ppm, and 75.23 ppm. The signal of C-2 was very weak. Examination of the CD spectrum of a mixture of Co(III)(phen)$_2$ and L-sorbose in H_2O showed that complex is formed in the conditions of our NMR experiments.

Structure simulation.—The molecular mechanics program was run on a CAChe Tektronix computer using MM2 parameters as described for other Co(III) complexes [5,11]. The parameters were: relaxation factor = 1; convergence to 10^{-3} kcal mol^{-1}, and energy terms include: bond angles and stretch, dihedral angles and improper torsions, intramolecular van der Waals, electrostatic, and hydrogen-bonding interactions. Binding of Co(III) at position 2 involves alkoxide oxygen, based on the charge of the dicationic complex in solution. The A-1,2-complex (Fig. 5) is predicted to be more stable than the 2,3- or the Δ-complexes.

Acknowledgements

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