Complexation of amino sugars with cobalt(III)bis(phenanthroline)

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The I_3^- salts are soluble in acetone and sparingly so in methanol, and I_3^- inhibits formation of Co(II) so that minor decomposition of a complex does not broaden its ^1H NMR signals.

The $(phen)_2$ complex of Co(III) with D-glucosamine (**1**) has been isolated as the sulfate and its stereochemistry examined [6], and there is limited evidence on the corresponding complex with D-mannosamine, (**2**) [5]. We have now extended the investigation to the corresponding complexes with D-galactosamine (**3**). These amino sugars are α- and β-mixtures in the $^4C_1$ conformation (Scheme 1) [1,7].

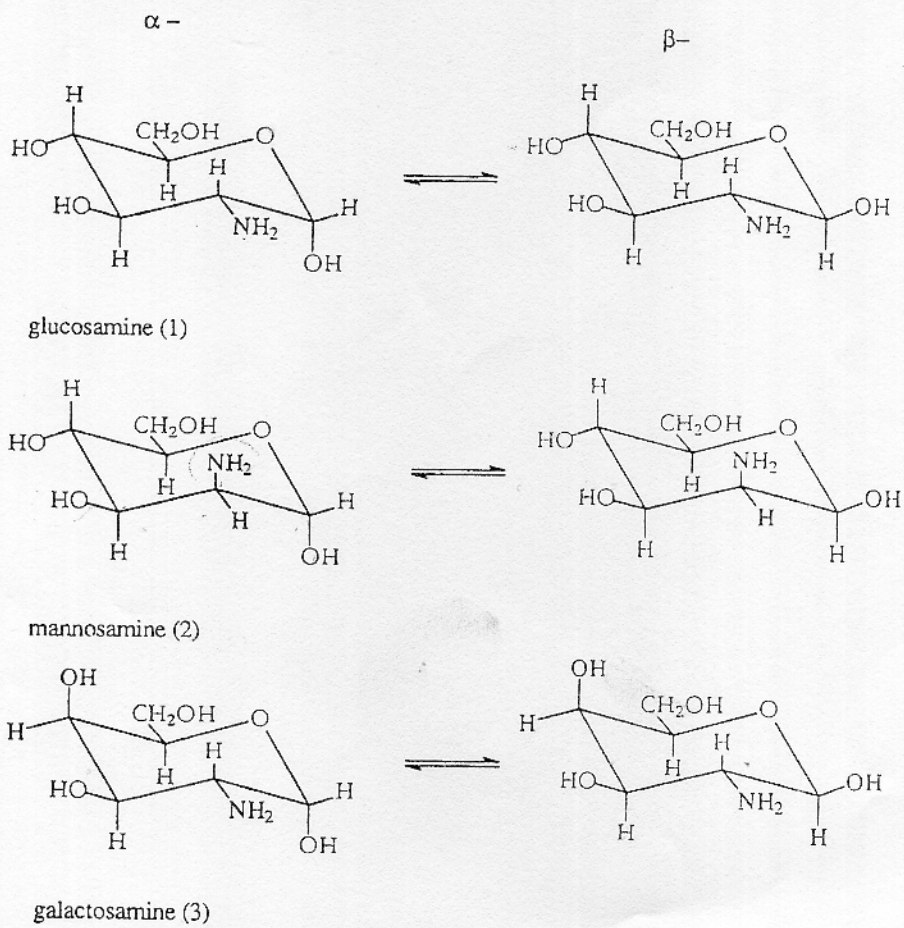
There is extensive evidence that formation of complexes from these, and similar ligands preferentially involves *cis*, *ax–eq* groups [7,8]. Therefore if the 1-OH (O^-) and 2-NH_2 groups are involved we would expect complexation with α-glucosamine (**1**), β-mannosamine (**2**), and α-galactosamine (**3**). The anomeric composition of the sugar residue can, in principle, be determined by ^1H NMR spectroscopy [9].

Coordination to metal cations increases acid dissociation constants of hydroxyl groups by 6–8 log units [3,10], depending upon the metal ion and solvent. Therefore the complexes with Co(III) are dicationic in mildly basic aqueous solution, but the analytical composition often corresponds to the existence of a trication due to ion-pairing and hydrogen-bonding in the crystals [3,4,6].

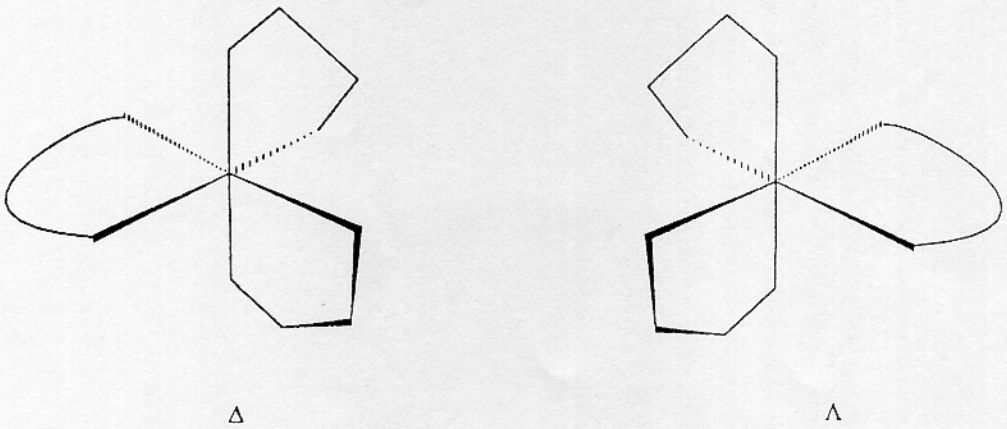
Octahedral complexes can have the Δ- or Λ-configuration at Co(III) (Scheme 2) and it can be determined from the signs and sequence of the CD or ORD signals, and we used the first method [11].

2. Experimental

Preparation of the complexes.—The complexes were prepared from $[Co(phen)_2Cl_2]Cl$ and the hydrochloride of the amino sugar by the general method used originally for preparation of glucosamine complexes [6]. These preparations may give mixtures of diastereomers with the Δ- and Λ-configuration at Co(III) and they can be separated chromatographically. Examples of preparations are given.



Scheme 1.



Δ Λ

Scheme 2.

The galactosamine complex was prepared in aqueous solution [6]; 0.5 mmol of $[Co(phen)_2Cl_2]Cl$ and an equimolar amount of D-galactosamine hydrochloride were dissolved in H_2O and the pH was brought to 8 (aq.NaOH) with stirring to a total volume of 50 mL. After 2 days at room temperature (~22 °C) fractions were separated on an SP Sephadex C-25 column with a KCl gradient of 0.1→0.3 M. Their CD spectra showed that the Δ-complex was eluted first, followed by material that contained the Λ- complex. Some dark-brown material remained on the column and a pale-yellow optically inactive material, probably $[Co(phen)_3]^{3+}$, was eluted after the other complexes.

Precipitation of the Δ- complex with KI_3 gave $[Co(phen)_2$D-galactosamine$](I_3)_3$: Calc: C, 20.70; H, 1.67; N, 4.0; Co, 3.37%: found : C, 20.98; H, 1.78; N, 4.0; Co, 3.56%. Based on the concentration of Co(III) in the eluant the yield of the Δ-complex relative to the starting $[Co(phen)_2Cl_2]^+$ was 36% and the cobalt content was determined by atomic absorption spectroscopy. A sample was also prepared by reaction in MeOH, although H_2O is the preferred solvent. Experiments were also made with sugar in excess and without chromatographic separation and the CD spectrum was similar in wavelengths to that of the isolated complex.

The mannosamine complex was prepared from 0.25 mmol of $[Co(phen)_2Cl_2]Cl$ and 0.25 mmol of D-mannosamine hydrochloride dissolved in 25 mL H_2O, pH 8.2, at ~22 °C. The following day the solution was transferred to an SP Sephadex C-25 column and elution was by gradient of 0.1→0.4 M KCl. Fractions were collected, their CD spectra were monitored and were characteristic of a Δ-complex which was precipitated by addition of KI_3 giving $[Co(phen)_2$D-mannosamine$](I_3)_3$: Calc : C, 20.70; H, 1.67; N, 4.0; Co, 3.37% : found : C, 20.90; H, 2.14; N, 4.0; Co, 3.54%. The yield of the Δ-complex in the eluant was 60%, based on estimation of the cobalt content.

The CD spectra of the reaction solutions before chromatography showed that the Δ- diastereomers predominated, as found earlier for the corresponding glucosamine complex [6].

Spectrophotometry.—The CD spectra were monitored in a Jobin–Yvon DC6 spectrometer and asbsorbance spectra were monitored in this instrument or in a Unicam UV3 spectrometer.

Spectra were monitored on the reaction mixture sometimes before chromatography, after chromatography, or as the triiodide salt of the complex dissolved in MeOH and treated with $Na_2S_2O_3$. Conditions were generally as described earlier [6] and in all cases the Δ- diastereomer was predominant.

Values of extinction coefficients, ε, and $\Delta\varepsilon$ for material which had been separated chromatographically were based on the Co content and those for the triiodide salt were calculated from the weight of material.

NMR spectroscopy.—^{1}H NMR spectra were obtained at 400 or 500 MHz in Varian Unity (Inova) spectrometers at 22 or 25 °C or at 300 MHz in a Bruker DRX300 spectrometer at 25 °C. Most data were obtained at 400 or 500 MHz.

Spectra of complexes isolated as triiodides were obtained with 0.01 M complex in $(CD_3)_2CO$. We had earlier reported that the mannosamine complex is soluble in CH_3CN [5] but the ^{1}H spectrum of the galactosamine complex in CH_3CN was that of the sugar, indicating that it is displaced by CH_3CN. Chemical shifts in $(CD_3)_2CO$ are referred to $(CD_3)(CHD_2)CO$, $\delta = 2.05$ ppm, corresponding to $\delta = 0$ for Me_4Si.

With the mannosamine complex in $(CD_3)_2CO$ there were weak signals of OH and NH_2. Fortuitously we used an old sample of $(CD_3)_2CO$ which was slightly moist and OH signals were relatively small [5]. Chemical shifts of the phenathroline ligands are high and there is no interference with the sugar signals.

With a mixture of the galactosamine complexes isolated as the triiodides we also saw weak signals of OH or NH_2. This triiodide is relatively labile and on addition of 3 vol% D_2O to $(CD_3)_2CO$ we saw, after 2 days, well defined signals of the sugar which, with those of the complex, were still sharp.

We also prepared the galactosamine complex in situ in D_2O with 0.01 M $Co(phen)_2$ and excess galactosamine hydrochloride, at pD ≈ 10, essentially as described for the glucosamine complex [12], except that the spectrum was badly degraded after 10–18 h. Initially chemical shifts of the unreacted excess α- and β- sugars were at: H-1, 5.25(4.51), H-2, 2.98 (2.82); H-3, 3.69 (3.54); H-4, 3.93 (3.86): values in parentheses are for the β anomer. Coupling constants were: $J_{1,2}$, 4 (8); $J_{2,3}$, 1 (10); $J_{3,4}$, 3.5 (3); $J_{4,5}$, 2.5 (3). These values are similar to those reported earlier for galactosamine [13] and differences in δ are due to the higher ionic strength induced by the Co(III) complexes and reference to $\delta_{HOD} = 4.8$ ppm rather than to $\delta_{TSP} = 0$ ppm, as in the earlier work.

3. Results

NMR spectroscopy.—Configurations at anomeric centers can be established from NMR coupling constants and chemical shifts [9], and we used two methods in examining the galactosamine complex. In the first we prepared it in situ (pD = 9.8), following the method used earlier with glucosamine [12]. With 0.01 M $Co(III)(phen)_2$ and a 5-fold excess of amino sugar we saw ^1H signals of a complex after 1.5 h, but after 14 h, signals were broadened by Co(II). Assignments of signals of H-1, H-2, H-3, and H-4 (Table 1) were confirmed by a simple COSY experiment. In a second experiment at pD = 10.2 we saw, after 1 h, signals of the original complex of H-1, H-2, and H-3 and weaker signals of a second complex. Both of these complexes were derived from the α sugar and based on the CD spectra the major complex had the D-configuration at Co(III). The chemical shifts are referred to $\delta_{HOD} = 4.80$ ppm and we neglect effects of pD and ionic strength.

Preparation of these complexes in situ has disadvantages, because the H-1 signal of the minor complex, which probably is Λ, is very close to that of α-galactosamine, and to avoid formation of Co(II), conversion into the complex was limited to 6% (relative to the sugar). We could make only approximate estimates of the relative amounts of the Δ- and the minor, Λ- complex, but initially Δ- is in ~2 -fold excess over Λ.

The galactosamine complexes are more labile than the glucosamine complexes for which, with 0.01 M reagents, pD = 9.8 we had obtained reasonable NMR spectra for up to 18 h after mixing [12].

In the second method we used isolated triiodide salts in $(CD_3)_2CO$ [5]. Formation of Co(II) with consequent line-broadening was not a problem,

Table 1
Chemical shifts, δ(ppm) and coupling constants, J(Hz) of the complexes

δ(ppm)	H-1	H-2	H-3	H-4	H-5	H-6	H-6′
Mannosamine-Δ^a	4.13d	3.64m	3.87dd	3.98Ψt	3.04m	3.68dd	3.57dd
Galactosamine-Δ^a	5.32d	3.30m	3.80dd	4.17m			
Galactosamine-Δ^b	5.13d	3.15dd	3.97m				
Galactosamine-Λ^b	5.27d	3.22dd	4.04m				
Glucosamine-Δ^b	5.38d	2.82dd					
Glucosamine-Λ^b	5.58d	2.91dd					
J(Hz)	**H-1,2**	**H-2,3**	**H-3,4**	**H-4,5**	**H-5,6**	**H-5,6′**	**H-6,6′**
Mannosamine-Δ^a	1.5	5.0	9.5	9.0	5.0	2.5	12.0
Galactosamine-Δ^a	3.0	9.5					
Galactosamine-Δ^b	3.5	ca.7					
Galactosamine-Λ^b	3.5	ca.7					
Glucosamine-Δ^b	3.5	11.5					
Glucosamine-Λ^b	4.0	10.0					

[a] As triiodide in $(CD_3)_2CO$, referred to $CD_3CO.CHD_2$, $\delta = 2.05$(ppm).
[b] complex prepared in situ, referred to HOD, $\delta = 4.8$(ppm).

and with a sample of the Δ-galactosamine complex in $(CD_3)_2CO$ and 3–10 vol% D_2O (to eliminate OH signals) we saw signals of the *a* and *β* sugars, but they were sharp after 7 days. Signals of H-1, H-2, H-3, and H-4 of the Δ- complex were assigned from the ^{1}H-COSY spectrum (Table 1). Chemical shifts differ slightly in $(CD_3)_2CO$ and D_2O, but coupling constants are similar. We also saw weak signals of the minor complex in a mixture of triiodide salts (Table 1). A solid sample of the minor complex, precipitated as the triiodide salt, had, after several weeks, ^{1}H signals of H-1 and H-2 which were the same, within experimental error, as those of the isolated Δ- complex (only these signals were identified because very little sample was available), showing that there was interconversion in the solid.

α-Mannosamine, in the $^4C_1$ conformation (**2**), cannot form a complex at 1-OH and 2-NH_2 (Scheme 1). The ^{1}H signals of the triiodide salt in $(CD_3)_2CO$ were assigned by homonuclear decoupling and a DQF-COSY spectrum (Table 1). Both *a*- and *β*- mannosamine have similar, low, $J_{1,2}$ coupling constants, but we assign configuration of the complex at position 1 as noted above. The coupling constants $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ (Table 1) are as expected for a chair conformation and are similar to those of *β*- mannosamine and its mannosammonium ion [13], indicating that complexation does not drastically change conformation of the pyranose ring. Complexation of *eq* 1-OH and *eq* 2-NH_2 in α-mannosamine would require a major change of conformation and be inconsistent with the observed coupling constants. We saw no signals corresponding to an uncomplexed 1-OH group. The mannosamine complex, as the triiodide, was shaken with D_2O for 30 min, which eliminates OH and NH_2 signals, and was then dissolved in $(CD_3)_2CO$ without introducing new ^{1}H signals. This result confirms earlier observations of the robust nature of the mannosamine relative to the other complexes [5], which allowed us to obtain the DQF- rather than the simple COSY spectrum.

Chemical shifts and coupling constants, where available, are summarized in Table 1, together with earlier data for the glucosamine complex [12]. Based on comparison with values of the coupling constants of the free sugars [13], complexation does not have major effects on conformations of the sugar moieties.

Some of the signals of the triiodide salt of the galactosamine complex were too overlapped to be identified in a simple COSY spectrum, but we saw well-defined doublets at 3.45 and 3.85 ppm with coupling constants of 12 Hz, and they are probably signals of H-6 and H-6′.

Examination of the ^{1}H NMR spectra of the galactosamine and glucosamine complexes after incomplete reaction of $Co(phen)_2$ and the amino sugars in D_2O reduces the chance of significant isomerization of the first-formed complexes, or formation of Co(II), which can occur under conditions which allow thermodynamic control of products. The use of relatively high concentrations of galactosamine hydrochloride increases the rate of formation of the complex, relative to its decomposition, that is, it favors kinetic over thermodynamic product control, but it increases the HOD signal and the high ionic strength broadens the NMR signals.

Absorption and CD spectra.—The mannosamine complex was isolated in solution by chromatography, and absorption and CD spectra were examined after estimation of the Co(III) content. The CD signals are given in Table 2 and the sign and sequence are diagnostic of the Δ- configuration at Co(III) [11]. A sample of the complex isolated as the triiodide salt was treated with sodium thiosulfate in methanol and the wavelengths of the CD signals in the accessible regions are very similar to the values in H_2O given in Table 2. The values of λ, Δε given in Table 2 differ slightly from the preliminary values [5] and there was a numerical error in the value of Δε at 223 nm.

It was more difficult to obtain reliable values of Δε for the Δ- complex of D-galactosamine with $Co(phen)_2$ because it is partially decomposed in aqueous solution, as shown by the ^{1}H NMR spectrum in D_2O-$(CD_3)_2CO$. This decomposition does not significantly affect the UV absorption spectrum which is governed largely by the $Co(phen)_2$ residue, and it does not affect the wavelengths of the positive and negative CD signals (Table 3). Decomposition therefore does not complicate assignment of the configuration at Co(III).

Values of Δε for the Δ- galactosamine complex given in Table 3 are probably low, as already noted, but relative values at the various wavelengths should be reliable. The CD spectrum of the minor complex in the UV region is characteristic of a Λ- complex.

Wavelengths corresponding to positive and negative CD signals of the Δ-galactosamine complex are similar to those of the Δ-mannosamine

complex (Tables 2 and 3) and to other mixed bis(phenanthroline) complexes of Co(III) [4,6,12].

Molecular modelling.—Structures of the complexes were simulated by using a Spartan program with PM3(tm) parameters. Examples of the predicted structures, including those of the glucosamine complexes are shown in Fig. 1, A–D. The earlier structure of the mannosamine complex, based on MM2 parameters [5], differs slightly from that now obtained by using PM3(tm) parameters, especially as regards some dihedral angles in the sugar residue. For example, predicted dihedral angles in the mannosamine complex, based on the PM3(tm) fitting, are: H-1–H-2, 32.5 (30.7); H-2–H-3, 39.0 (31); H-3–H-4, 170 (172); H-4–H-5, 178 (177). Values in parentheses were obtained by using the MM2 fitting [5]. Structures are those of dicationic complexes, which should be present in water at pH 8–10, [3,6,10] but simulated structures with coordination of 1-OH to Co(III) are similar to those shown. We did not simulate structures of complexes of β-glucosamine or galactosamine, which are excluded by the NMR data. Our simulations do not take into account hydration of OH or NH_2 groups or ion-pairing. Resimulations were used to avoid false minima and for the mannosamine complex we also used MM2 parameters to simulate the structure of the hypothetical complex with the α- sugar in the unfavorable chair conformation, and then changed the configuration at C-1 to that of the β sugar with PM3(tm) parameters. This procedure generated the same simulated structure as that from the original simulation. Results for the simulations accord with our NMR data for the β-mannosamine complex with axial hydrogens at positions 1,3, 4, and 5 of the pyranose residue. A hypothetical complex with α-mannosamine is predicted to have a skew conformation with the following dihedral angles: H-1–H-2, 164; H-2–H-3, 38.6; H-3–H-4, 138; H-4–H-5, 171°. These values are inconsistent with the observed coupling constants (Table 1). The bond angle of Co(III) to the α sugar is predicted to be 93.7°, and somewhat larger than that for an undistorted octahedral complex.

The MM2 parameters are generated from data on properties of organic molecules with some data on inorganic complexes, and the PM3(tm) semi-empirical treatment takes into account orbital and nonbonding interactions based on parameters consistent with experimental data from a larger number of compounds, and to this extent should be the better approach for complexes of transition metals. Problems in modeling structures of complexes of transition metals with ligands of biological interest have been discussed, especially as regards the problem of false minima [1b], and allowance for solvent–solvent interactions. As a result modeling is useful in so far as it complements experimental data.

4. Discussion

Structures of complexes.—The favoured Δ-configuration at Co(III) is demonstrated by the sequence of the CD signals [11]. We saw no evidence for a Λ- complex from D-mannosamine, but a Λ- complex of $Co(phen)_2$ with D-glucosamine has been isolated [6], and D- galactosamine gives a minor, labile, Λ- complex (Table 1).

Table 2
Absorption and circular dichroism spectra of the mannosamine complex [a]

Absorbance		CD	
λ nm	log ε	λ nm [b]	Δε
		223 (226)	−78.0
		235 (236)	+20.0
272 [c]	4.72	268 (269)	+67.0
300sh	≈4.3	281 (282)	−78.0
320sh	≈3.9	316 (319)	+12.0
391sh	≈2.5	389 (390)	+1.1 [d]
491	2.23	502 (505)	−3.0 [d]

[a] Measured in the column eluant after analysis of cobalt.
[b] Values in parentheses are wavelengths of CD signals of the triiodide salt of the complex.
[c] There is strong absorbance at lower wavelengths.
[d] Values of Δε of the triiodide salt are +0.95 and −3.0 at 390 and 505 nm respectively.

Table 3
Absorption and circular dichroism spectra of the D-galactosamine complex [a]

Absorbance		CD	
λ nm	log ε	λ nm [b]	Δε
—	—	224	−15.0
—	—	235 (240)	+17.0
270 [c]	4.540	266 (265)	+1.0
295sh	4.00	280 (284)	−17.0
319sh	4.00	317 (320)	+4.0
		357 (356)	−1.0
		417 (419)	+0.8
480	2.10	500 (503)	−1.6

[a] Measured on column eluant after analysis of cobalt.
[b] Values in parentheses are wavelengths after treatment of the triiodide salt with sodium thiosulfate; the Λ-complex has CD signals at λ nm; 239(-); 266(-); 320(-).
[c] There is a strong absorbance at lower wavelengths.

The NMR spectra are similar for complexes prepared in situ in D_2O, or isolated as triiodides (Table 1), and differences in chemical shifts are due to medium effects. We conclude that complexation always involves *cis* hydroxy and amino groups at positions 1 and 2 respectively, because complexation at positions 2 and 3, or elsewhere, would allow existence of two H-1 signals, characteristic of *a* and β anomers [9]. In the glucosamine and galactosamine complexes, as with parent pyranose sugars, the anomeric composition is demonstrated by the values of $J_{1,2}$ [9]. Complexation with α-mannosamine in its unfavorable, $^1C_4$, conformation is excluded by consideration of the coupling constants (Table 1) which are as expected for complexation with the β anomer (Scheme 1). It is possible that *a*-mannosamine complexes in a twisted conformation, but in that event it is difficult to envisage structures consistent with the observed coupling constants.

In galactosamine complexes, small signals of H-1 of the β anomer could be obscured by the signal of HOD, unless it is eliminated in a DQF-COSY spectrum [14]. As noted, acquisition of this spectrum is too slow for it to be useful with labile complexes. However, we do not have serious interference by HOD in $(CD_3)_2CO$ where we see only single signals of H-1 and H-2.

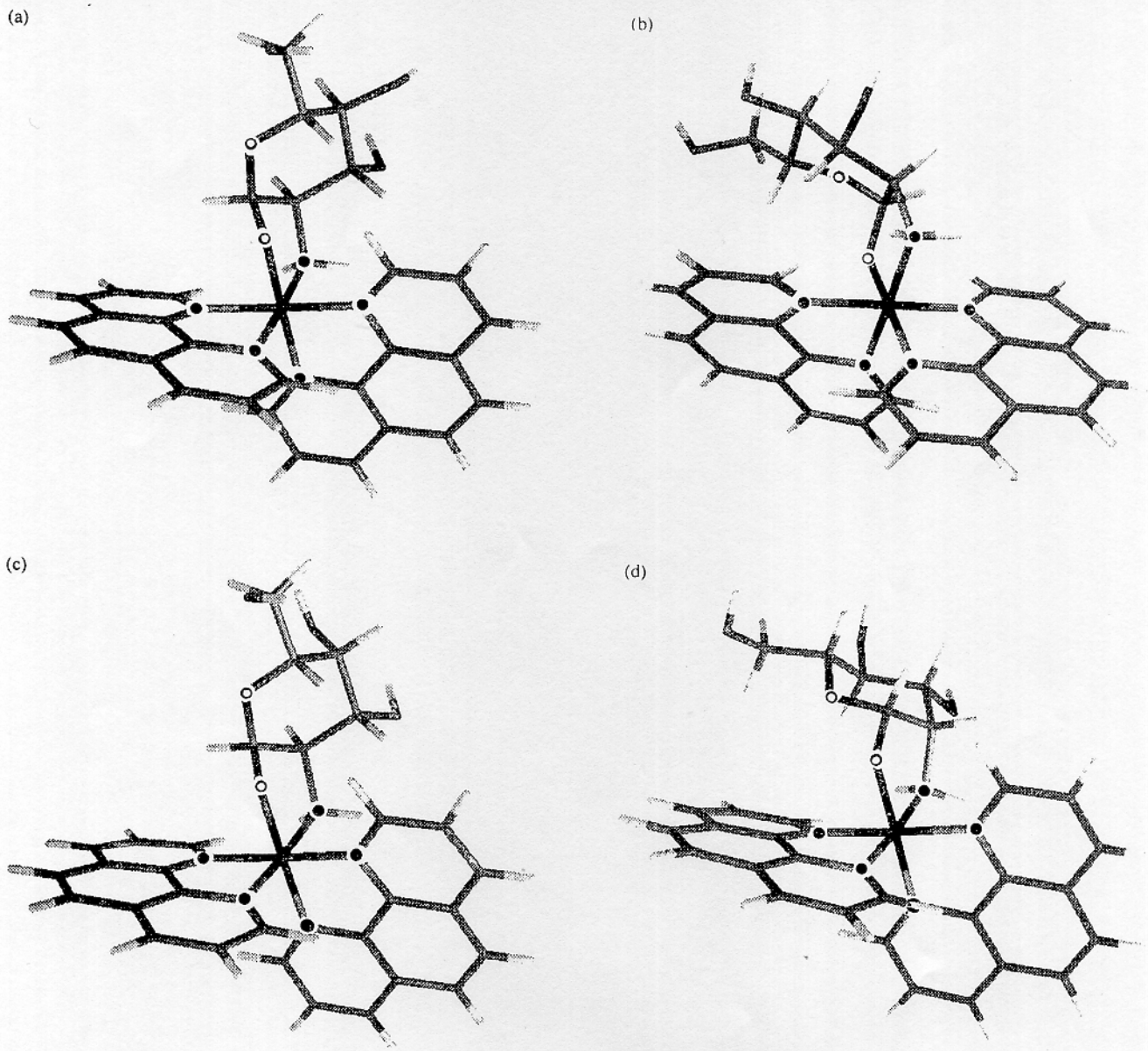
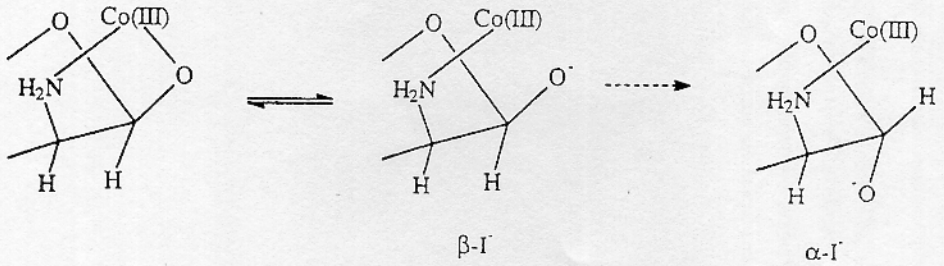
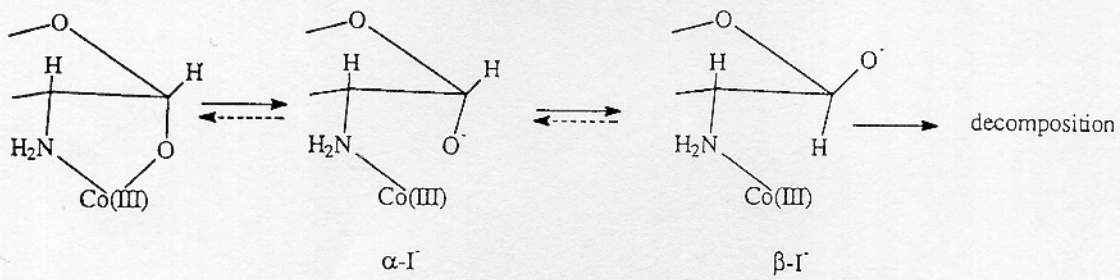


Fig. 1. Simulated (PM3-tm) structures of the dicationic Co(III) complexes, from the upper left: (a) Δ-D-glucosamine Co(III) $(phen)_2$; (b) Λ-D-glucosamine Co(III) $(phen)_2$; (c) Δ-D-galactosamine Co(III) $(phen)_2$; (d) Δ-D-mannosamine Co(III) $(phen)_2$. In the Δ-complexes oxygen-1 is in front of the plane of the paper, in the Λ-complex it is behind.

mannosamine complex (stable)



glucosamine/galactosamine complex (relatively unstable)



phenanthroline ligands, parts of the sugar and charge on the Co(III) residue are omitted for clarity.

Scheme 3.

The initial reactions with glucosamine and galactosamine give both Δ- and minor complexes, with kinetic preferences for the former [6], but, as in other systems, the sequence of the CD signals [11] shows that one diastereomer becomes dominant with time. We saw no evidence for even initial formation of a Λ- complex of mannosamine.

Predicted structures of the Δ- complexes of $Co(phen)_2$ with α-D-glucosamine and galactosamine are similar (Fig. 1), indicating that the configuration at C-4 does not have a major effect on conformations of the complexes, in agreement with the coupling constants (Table 1), probably because C-4 is relatively remote from the coordination sites.[1] In these complexes, the planes of the pyranose residues are shown as tilted above the equatorial plane of O^- and NH_2 with Co(III) (Fig. 1). The Co(III)–O bond is in the plane of the 'upper' phenanthroline. However, in the corresponding Λ-complexes, as shown for the Λ-glucosamine complex, the planes of the pyranose residues are tilted below the equatorial plane of O^- and NH_2 with Co(III) (Fig. 1). As a result the edge of the 'lower' phenanthroline ring is relatively close to the pyranose residue. The different stabilities of the Δ- and Λ- complexes are probably related to these differences in the relative orientations of the pyranose and phenanthroline residues.

In the Δ-mannosamine complex the pyranose residue is tilted down (Fig. 1), and is away from the face of the 'lower' phenanthroline ring which minimizes non-bonding interactions within the complex. In the corresponding hypothetical Λ-complex the edge of the phenanthroline ring is oriented toward the pyranose residue (representation not shown), and we assume that this geometry destabilizes the Λ- relative to the Δ- complex.

These simulations do not include solvation of the sugar residues, which may affect their conformations [1b,15,16]. However, in the mannosamine

[1] The simulated structures (Fig. 1) are viewed from directions chosen to avoid excessive overlap of the pyranose and phenanthroline residues. It is difficult to select viewing angles which clearly show the pyranose residues in chair conformations without having one phenanthroline ring obscure the other.

and galactosamine complexes, and probably also in the glucosamine complex, equilibria favor the Δ- over the Λ- complex both in solution and in the crystal, based on the CD spectra.

These Co(III) complexes decompose in water with loss of the sugar residue and formation of Co(II) species, but these reactions are much less evident with the mannosamine than with the other complexes. Our tentative explanation for these differences is based on the observation of complexation with the α anomers of glucosamine and galactosamine and with β-mannosamine. The first step of decomposition in water probably involves opening of the Co(III)–O bond at position 1 of the sugar. In complexes of α-glucosamine and galactosamine the conformation at C-1 favors opening of the pyranose ring in α-I^- allowing anomerization and interconversion of α-I^-, and the non-complexing species, β-I^- (Scheme 3). However, the corresponding species, β-I^-, in the β-mannosamine complex has the appropriate geometry for ready reformation of the Co(III)–O bond, rather than anomerization. In addition, in water and other protic solvents solvation favors the equatorial over the axial O^-(OH) [17], and should disfavor conversion of β-I^- into α-I^- in the β-mannosamine complex, as compared with conversion of α-I^- into β-I^- in the α-glucosamine and galactosamine complexes. The proposed reaction sequence is shown in Scheme 3 where the mannosamine complex generates β-I^- which readily recloses, but the other complexes generate α-I^- which can anomerize to β-I^-, leading to decomposition, rather than regeneration of the complex.

Kozlowski et al. noted that complexes of metal ions with mannose derivatives are more stable than with the corresponding derivatives of glucose or galactose [2a], although positions of complexation are uncertain. Our results accord with these data.

The electronic spectra of these and similar Co(III) complexes has been discussed, based on standard treatments [18]. The visible CD signals are under the d–d absorbances of Co(III) at ~500 nm, as in the complexes with amino sugars and polyols [4,6,18–20]. The absorbance and CD signals in the uv region are dominated by the strong absorption of the phenanthroline ligands. The maxima, and shoulders, in the absorption spectra (Tables 2 and 3) are at wavelengths similar to those seen with other complexes, and the CD signals are under the known absorptions of the phenanthrolines [18].

5. Conclusions

Configurations of complexes of Co(III) with bis(phenanthroline) and amino sugars at Co(III), and at the anomeric center, can be determined by a combination of CD and NMR spectroscopy. However, decomposition of the complexes generates Co(II) species and complicates use of ^{1}H NMR spectroscopy for structural elucidation. Water-insoluble complexes can be isolated with I_3^- as counter ion and the predominant crystalline Δ-complexes retain the configuration at Co(III), and analytical composition, for several months, whereas the sulfates decompose in the solid [6].

Acknowledgements

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