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Complexes of cobalt(III) with D-glucosamine and amines

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ABSTRACT

D-Glucosamine and ammonia, 1,2-ethylenediamine, or 1,10-phenanthroline form complexes with Co(III) *. The complexes are: $[Co(NH_3)_3 \cdot H_2O \cdot$ D-glucosamine$]^{3+}$, $[Co(en)_2 \cdot$ D-glucosamine$]^{2+}$ and $[Co(phen)_2 \cdot$ D-glucosamine$]^{3+}$. Formation of the last two complexes is stereospecific with Co(III), with predominance of the Δ over the Λ diastereomer. The Δ and Λ diastereomers of the ethylenediamine and phenanthroline complexes with D-glucosamine were separated and their configurations about Co(III) assigned from the CD and ORD spectra. The ethylenediamine complex has $pK_a \sim 3.4$ and is more acidic than the other complexes, pointing to coordination of the alkoxide residue at position 1 of glucosamine.

INTRODUCTION

Amino sugars are effective bidentate ligands towards a variety of metal ions[1–7]. In D-glucosamine, the α and β anomers are in equilibrium[8,9] in a ratio of $\sim 3:2$ (based on the NMR spectrum of a relatively concentrated solution at 70°C).

The bonding of metal ions generally involves groups at positions 1 and 2, although if position 1 is blocked, for example by *O*-alkylation, bonding may[6] involve position 3. If the ligands, for instance, hydroxyl groups, have the *ax, eq, ax* orientation (*cis,cis*) three groups may bond to the metal ion[7,10]. Metal ions may therefore bond to glucosamine at the equatorial 2-amino group and the 1-hydroxyl group of the α or β anomer. Coordination of the β anomer at the 1 and 2 positions involves two equatorial groups, which should be less favorable than bonding to the *cis* OH and NH_2 groups of α-glucosamine. However, coordination

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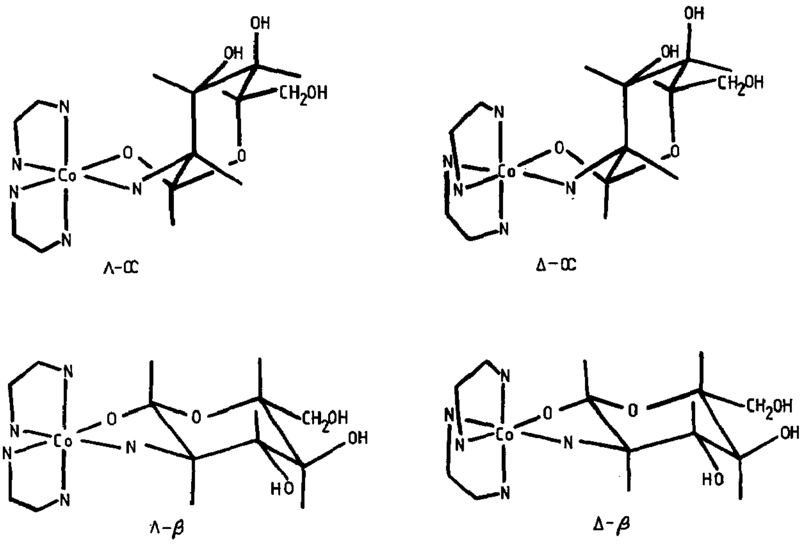
* Abbreviations: 2-amino-2-deoxy-D-glucose, D-glucosamine; 1,2-ethylenediamine, en; 1,10-phenanthroline, phen.



Scheme 1.

of the α anomer may create unfavorable interactions between the sugar and other ligands to the metal, and coordination of the NH_2-2 and OH-3 groups[6] also has to be considered.

The configuration about Co(III) may be assigned by comparison of the optical rotatory dispersion (ORD) and circular dichroism (CD) spectra with those of complexes of known configuration[11–13].

We have investigated the formation and structure of complexes of carbohydrates, and amino or hydroxy acids, with Co(III), generally with ammonia or bidentate amines. The present work examines complexes of Co(III) with D-glucosamine and ammonia, ethylenediamine and phenanthroline in order to determine whether the reaction is stereoselective in the last two systems, leading to Λ or Δ diastereomers at Co(III), based on a pseudo three-fold axis of symmetry (Scheme 1).

EXPERIMENTAL

Materials.—Complex **1** $[Co(NH_3)_3 \cdot H_2O \cdot$ D-glucosamine$]_2(SO_4)_3 \cdot 3H_2O$ was prepared as described[14].

The bis(ethylenediamine) · D-glucosamine complex (**2**), $[Co(en)_2 \cdot$ D-glucosamine$]Cl_2 \cdot 4H_2O$ was prepared as a mixture of Δ and Λ diastereomers from D-glucosamine hydrochloride (2.8 g, 8 mmol) and $[Co(en)_2\ Cl_2]Cl$ (1.7 g, (8 mmol) in 25 mL of H_2O. The pH was brought to 8 (NaOH) and the solution volume was diluted to 100 mL. The solution was kept for 4 h at 40°C. These conditions appeared to be optimum. The solvent was then evaporated in a stream of air and

Me_2CO (170 mL) was added to give an oily red paste which was redissolved in H_2O (5–10 mL). The pale-rose complex was precipitated by adding EtOH (80 mL) dropwise, washed with small amounts of EtOH, and was dried in a vacuum desiccator; yield 3.5 g (87%). Anal. Calcd: C, 24.03; H, 7.20; N, 14.02. Found: C, 24.08; H, 5.79; N, 13.64. The hydrogen content of this and similar complexes varied from sample to sample, probably because of changes in the number of water molecules of crystallization.

The diastereomers were separated chromatographically on a column of SP Sephadex C-25 (Na^+ form, 1.5 × 140 cm) with 500 mg of complex in 20 mL of H_2O. Two well-defined orange bands separated and a small amount of colored material remained at the top of the column. The complexes were eluted by using a K_2SO_4 gradient (0.025–0.45 M) and fractions were monitored by their ORD and absorbance spectra and their Co content (determined by atomic absorbance spectrometry). Combined fractions were concentrated in a stream of air, desalinated on Sephadex G-10, and the diastereomers were isolated, as described, by addition of EtOH. The ratio of the isomers in the eluate was $\Delta:\Lambda = 7:3$. Anal. Δ: $[Co(en)_2 \cdot$ D-glucosamine$]SO_4 \cdot 4.5H_2O$: Calcd: C, 22.46; H, 6.92; N, 13.10. Found: C, 22.4; H, 6.04; N, 13.00. Λ: $[Co(en)_2 \cdot$ D-glucosamine$)SO_4 \cdot 6.5H_2O$: Calcd: C, 20.97; H, 7.17; Co, 10.31; N, 12.23. Found: C, 21.38; H, 5.17; Co, 10.25; N, 12.36.

The bis(phenanthroline) complex $[Co(phen)_2 \cdot$ D-glucosamine$]_2 \cdot (SO_4)_3 \cdot 3H_2O$ (**3**) was prepared as a mixture of Δ and Λ complexes from *cis*-$[Co(phen)_2Cl_2]Cl \cdot 3H_2O$ (ref. 15) (0.200 g, 3.45 mmol) and D-glucosamine hydrochloride (0.075 g, 3.45 mmol) in 30 mL of H_2O, pH 8 (NaOH). The solution was kept at room temperature for 4 days at constant pH and the ORD spectrum (476–550 nm) was monitored. When the optical activity became constant the solution was passed through Dowex 14 (SO_4^{2-}) resin. The solution, which contained no Cl^-, was concentrated in vacuo to give coffee-colored crystals, (yield ~55%), which were dried in a dessicator. Anal. Calcd: C, 46.88; H, 3.93; Co, 7.67, N, 9.11; S, 6.26. Found: C, 46.32; H, 4.35; Co, 7.36; N, 9.20; S, 5.93.

The diastereomers were separated as already described, except that SP Sephadex C-25 was used in the potassium form. The first material eluted was optically inactive. The two diastereomers then followed and fractions were monitored as already described. In this case, the crystalline diastereomers could not be isolated. They were characterized in solution by determination of the Co content and measurement of the absorbance and CD spectra, which showed that the ratio of the second to the first chiral material eluted was 16:1.

Chromatography of $[Co(NH_3)_3H_2O \cdot$ D-glucosamine$]_2(SO_4)_3$ (**1**) gave only one product.

Conductivity.—Conductivities of aqueous solutions of complexes **1**, **2**, and **3** were measured as described earlier. They are consistent with complexes **1** and **3** having a charge of 3^+, and complex **2** a charge of 2^+, in agreement with analyses of the solids. A pH titration of the diastereomeric mixture of the bis(ethylenediamine) complex **2** gave an apparent pK_a of 3.4.

Spectrophotometry.—The UV-visible absorbance spectra in water were monitored in a Zeiss PM Q-2 or a Cary 11 spectrophotometer. The absorbance spectra of the Δ and Λ diastereomers were very similar.

The ORD and CD spectra were monitored on a Cary 60 spectropolarimeter and optical activity was also monitored at various wavelengths on a Perkin–Elmer polarimeter with an attached monochromator. These measurements were performed using 10^{-2}–10^{-4} M aqueous solutions at room temperature (20°C). The CD spectrum of the ammonia complex **1** was examined qualitatively by using a Shimadzu spectrophotometer, which gave[14] unreliable values of $\Delta\varepsilon$. The ORD spectra of the three complexes (data not shown) are consistent with the CD spectra. Decomposition of the ammonia complex **1** in the course of spectral measurements was decreased by adding $(NH_4)_2SO_4$.

RESULTS AND DISCUSSION

The charge and composition of the ammonia and bis(phenanthroline) complexes (**1** and **3**) show that glucosamine is complexed to cobalt through an OH group, but in the bis(ethylenediamine) complex **2** coordination is through an alkoxide group, except at low pH. The source of these differences in acidity is discussed later.

The CD spectrum of $[Co(NH_3)_3 \cdot H_2O \cdot$ D-glucosamine$]_2(SO_4)_3 \cdot 3H_2O$ (**1**) is illustrated in Fig. 1. The visible absorbance spectrum (λ_{max} 525 nm) covers two CD bands, positive at 500 and negative at 570 nm. The spectra are similar to those found for the D-ribose complex[16] $[Co(NH_3)_4 \cdot$ D-ribose$]^{3+}$ in which two oxygen atoms are complexed *cis* to cobalt. If oxygen atoms were disposed *trans* at Co(III), the energy levels could be reversed (see later for assignments), in which case the CD spectrum under the first absorption band would be of opposite sign to that observed. The spectra should also be different if one oxygen and five nitrogen atoms were bonded to Co(III).

The presence of a fifth amino ligand in the coordination sphere of Co(III) in the Δ and Λ isomers of $[Co(en)_2 \cdot$ D-glucosamine$]^{2+}$ (**2**) gives a pronounced hypsochromic shift in the visible absorbance spectrum, and the λ_{max} is 490 nm (Fig. 2).

The bis(phenanthroline) complex $[Co(Phen)_2 \cdot$ D-glucosamine$]^{3+}$ (**3**) displays a strong $\pi \rightarrow \pi^*$ absorbance of the phenanthroline ligands in the UV and a visible absorbance at 500 nm, with a hypsochromic shift due to the ligands (Figs. 3 and 4.).

Assignment of structures.—Configurations of the glucosamine complexes at Co(III) may be assigned by comparison with optical properties of complexes of known structure[11–13]. No evidence was observed for anomer formation or mutarotation of the glucosamine residue in these complexes, and the high acidity of the bis(ethylenediamine) complex (**2**) presumably involves deprotonation of the HO-1 group.

The anomeric OH group should be more acidic than the other OH groups by at least one order of magnitude, based on comparisons with data for other sugars[17].

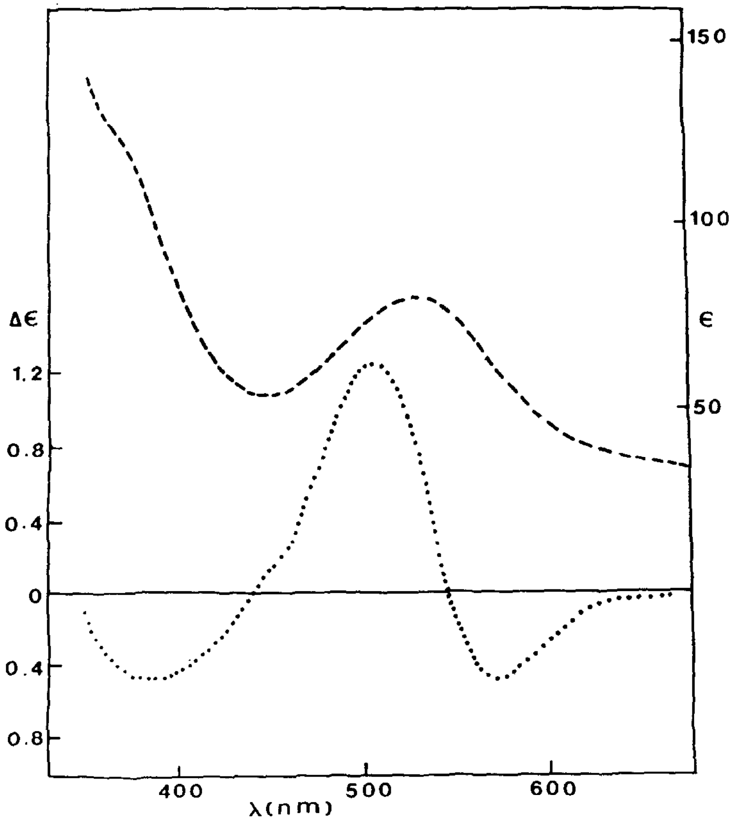


Fig. 1. The visible absorbance (— — —) and circular-dichroism spectra (· · · · ·) of [Co(NH$_3$)$_3$·H$_2$O·[D-glucosamine]$^{3+}$.

However, this evidence does not distinguish between bonding of the α or β anomers, although it may be safely assumed that coordination to Co(III) is at positions 1 and 2 in the ethylenediamine complex (**2**).

Most complexes of D-sugars and tetrammine Co(III) exhibit similar patterns of CD spectra under the first *d–d* absorbance band of Co(III) with two signals: a negative one at ~550 nm and a positive one at ~500 nm. This pattern is generally independent of the number of asymmetric centers, of the nature of the sugar, and of its functional groups. The Co(III) in all of these complexes is coordinated to four nitrogen atoms and two *cis*-disposed oxygen atoms. The T1g state splits into the $^1A_2$ and ^1E states under holohedrized D$_{4h}$ microsymmetry. Their energies correspond to: (10 Dq – C) and (10 Dq – C – $\frac{35}{4}$Dt), respectively[18]. The location and separation of both states depend on the value of Dt, which may be expressed in terms of the equatorial and axial contributions at Co(III) of Dq^N and Dq^0. The separation is then $\frac{2}{7}$(Dq^0 – Dq^N). Because Dq^N is always larger than Dq^0 (refs. 19 and 20), the $^1A_2$ state is of lower energy than the ^1E state. Therefore, the first (negative) CD signal corresponds to the $^1A_2$ state, and the second

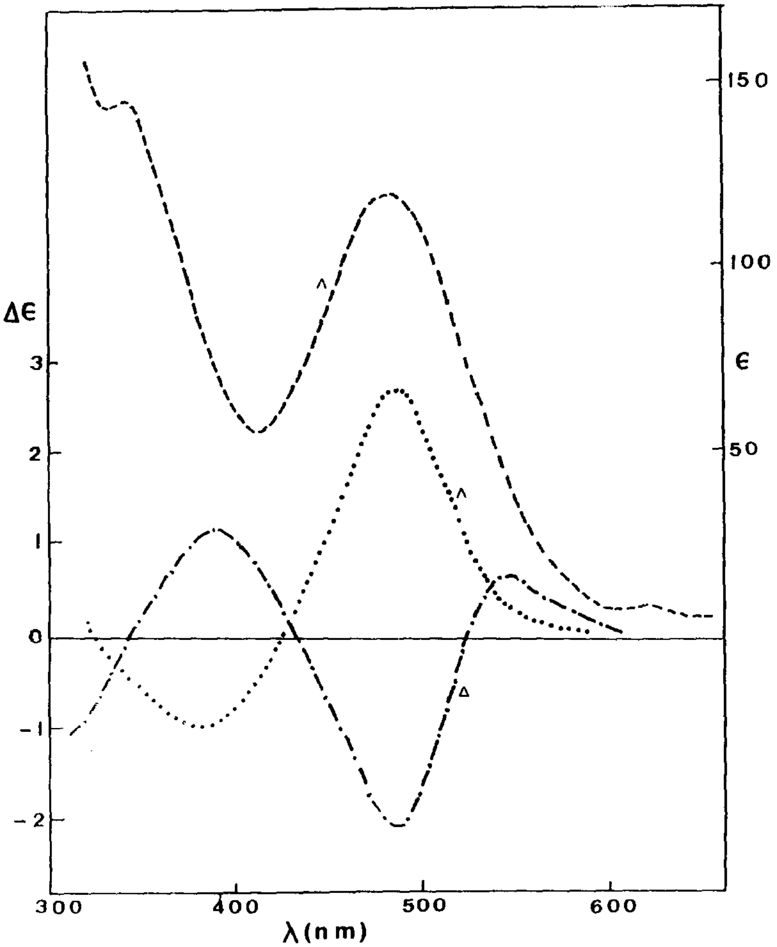


Fig. 2. The visible absorbance (— — —) and circular-dichroism spectra (–·–·– and ·····) of Δ-[Co(en)$_2$·D-glucosamine]$^{2+}$ and of Λ-[Co(en)$_2$·D-glucosamine]$^{2+}$.

(positive) one to the ^1E state, which is dominant and is also associated with the higher amplitude, positive, ORD Cotton effect.

Spectra of [Co(NH$_3$)$_3$ · H$_2$O · D-glucosamine]$^{3+}$ (**1**) (Table I) are consistent with coordination of the α or β anomer of glucosamine or of the NH$_2$-2 and HO-3 groups to Co(III). The arrangement of the other ligands is not known, except that the CD spectrum suggests[16] that the OH of the sugar and H$_2$O are *cis* at Co(III).

In considering configurations of the ethylenediamine and phenanthroline complexes (**2** and **3**), we first analyzed the CD bands that are under the *d–d* absorbances of Co(III) at ~ 500 nm.

In [Co(en)$_2$ · D-glucosamine]$^{2+}$ (**2**) the energy difference between the $^1A_2$ and ^1E states is smaller than in complexes having vicinal oxygen ligands from a sugar, and corresponds[18] to $\frac{1}{7}$(Dq^0 − Dq^N). The Δ complex has two CD signals under the first absorption band of Co(III) which correspond to the $^1A_2$ state with the lower, and the ^1E state with the higher energy. The Λ complex shows only one positive CD signal, which corresponds to the ^1E state (Fig. 2). This difference between the isomers at Co(III) may be ascribed to the sum of the configurational effect on the chelate rings around Co(III) and the conformational effect on the chelating carbohydrate.

In Co(III) complexes of phenanthroline and D-glucosamine, both Δ and Λ isomers show only one CD signal under the first visible absorption band of Co(III), which corresponds to the ^1E state (Fig. 3). The mixture of diastereomers shows CD signals in the UV region under the *p* band of phenanthroline. Comparison of these signals with those of the diasteromers (Fig. 4) shows that the Δ form is in

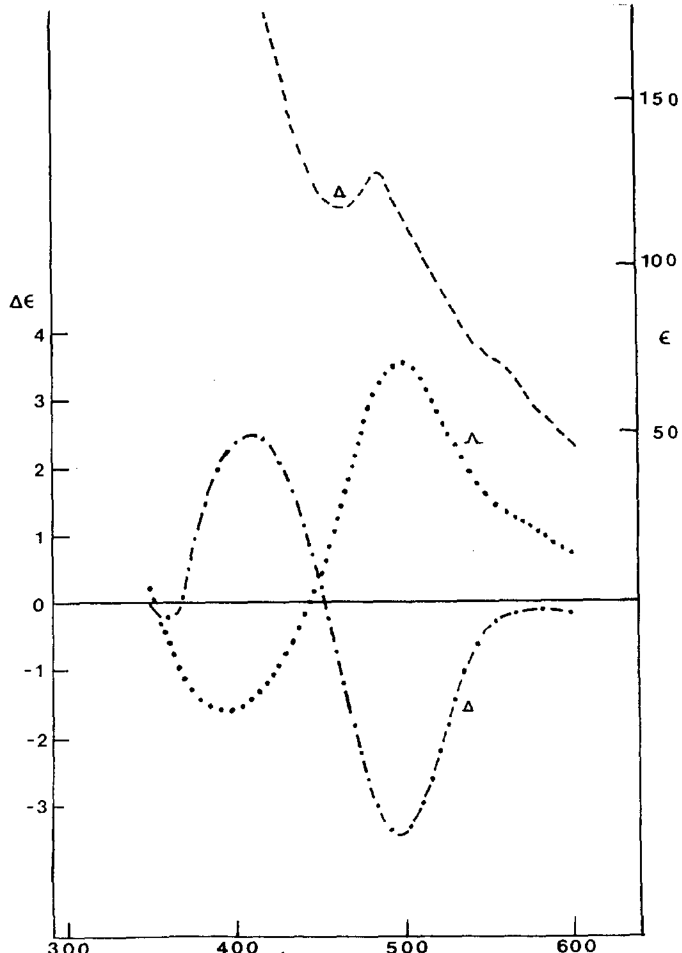


Fig. 3. The visible absorbance (———) and circular-dichroism spectra (-·-·- and ·····) of Δ-[Co(phen)$_2$·δ-glucosamine]$^{3+}$, and of Λ-[Co(phen)$_2$·D-glucosamine]$^{3+}$.

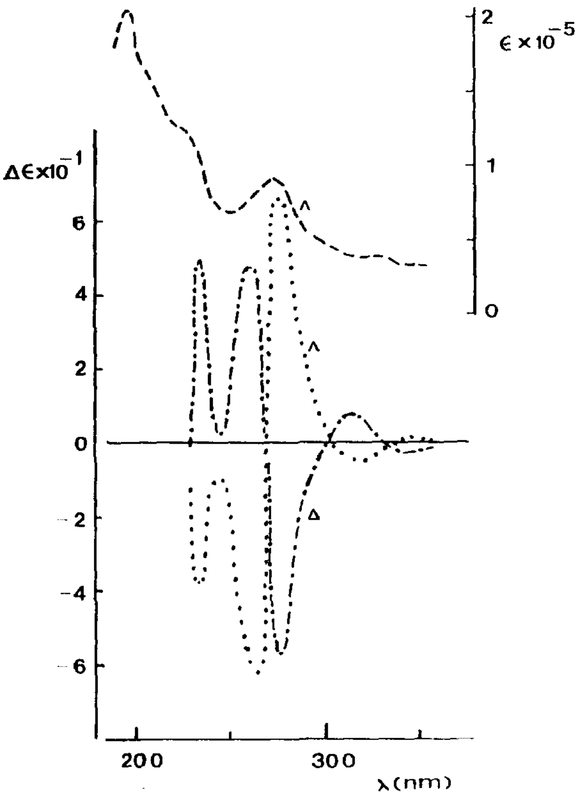


Fig. 4. The UV absorbance (———) and circular-dichroism spectra (–·–·– and ······) of Δ-[Co(phen)$_2$·D-glucosamine]$^{3+}$ and of Λ-[Co(phen)$_2$·D-glucosamine]$^{3+}$.

excess over the Λ isomer, based on comparisons with CD spectra of complexes of known configuration.

Inspection of models suggests that there are differences in conformations of chelate rings involving 1,2-diamines and either amino acids or sugars. The chelate ring involving a sugar residue should be less flexible than those of acyclic amino acid ligands.

The Δ complex of [Co(en)$_2$ · D-glucosamine]$^{2+}$ (**2**) is formed in a larger amount than the Λ diastereomer, as shown by chromatography. The relative amounts may also be calculated from the CD spectra of the mixture and of the pure diastereomers in the visible region. The ratio of Δ: Λ 7:3 agrees with the value determined by chromatography.

Examination of the CD signals of a freshly prepared solution of [Co(phen)$_2$ · D-glucosamine]$^{3+}$ (**3**) shows that the minor diastereomer has the Λ configuration at Co(III) and the ratio Δ:Λ is 7:3. Marked steric repulsion between the bulky phenanthroline groups and hydrogen atoms of the sugar should lead to a greater difference in stability than with the ethylenediamine complexes. Consistently the

TABLE I

Electronic spectra and circular dichroism of the complexes [a]

Complex	λ_{max} (nm)	ε	λ (nm)	Δε
$[Co(NH_3)_3 \cdot H_2O \cdot$ D-glucosamine$]^{3+}$	525	82	570	−0.45
			500	+1.30
	~376 [b]	120	385	−0.43
Δ-$[Co(en)_2 \cdot$ D-glucosamine$]^{2+}$	490	112	540	+0.62
			480	−2.1
	~390 [b]	91	390	+1.2
Λ-$[Co(en)_2 \cdot$ D-glucosamine$]^{2+}$	480	123	480	+2.7
	~340 [b]	148	380	−0.89
Δ-$[Co(phen)_2 \cdot$ D-glucosamine$]^{3+}$	484	121	495	−3.4
			410	+2.5
			313	+8.2
	273	66,000	277	−58.6
			262	+48.3
	~225 [b]	96,500	236	+49.4
Λ-$[Co(phen)_2 \cdot [$D-glucosamine$]^{3+}$	484	120	495	+3.5
			390	−1.5
			320	−5.6
	271	89,000	278	+66.4
			265	−62.8
	~233 [b]	150,000	234	−35.8

[a] Units for ε and Δε are in cm^{-1} mol^{-1} L. [b] Shoulder.

ratio of Δ and Λ complexes estimated chromatographically with analysis of the cobalt content of the eluants is Δ : Λ 16 : 1, which suggests that the diastereomers are interconverting in the column to give the Δ isomer almost quantitatively. In addition, there is irreversible disproportionation to give the tris(phenanthroline) complex.

The solid decomposes over a period of several months, loses optical activity, and finally gives Co(II) complexes. It is much less stable than the ethylenediamine complex **2**.

These structural assignments are based on spectral analysis in the region of the *d–d* transitions at ~500 nm. However, for the tri(ammine) and bis(ethylenediamine) complexes, signals at lower wavelengths (320–400 nm) also have to be considered. There are shoulders in the absorbance spectra of complexes **1** and **2** at 340–390 nm, and under these bands there are relatively strong CD signals (Figs. 1 and 2 and Table I). Circular dichroism signals in this region due to *d–d* transitions should be very weak, because they are magnetically and electrically forbidden. However, if *d–d* transitions couple with charge-transfer transitions of similar energy, they gain rotary strength. There is precedent for this assignment on other cobalt(III) complexes with water and sugar or malate ligands[16].

These charge-transfer transitions depend upon interactions between *p* orbitals of oxygen and orbitals of Co(III), and it appears that conformations of glucosamine and ribose[16] complexes of Co(III) favor this interaction. The situation is different for the Δ and Λ phenanthroline complexes.

There are the usual strong excitonic CD signals, but signals at 313–320 and ~ 235 nm are also seen (Fig. 4 and Table I). There is an ill-defined shoulder in the absorbance spectrum at 320–325 nm which can be seen only on an expanded scale. The CD signals at 313–320 and ~ 235 nm correspond to $\pi \rightarrow \pi^*$ transitions that are polarized along the short axis of phenanthroline, whereas the stronger signals at -277 and ~ 263 nm correspond to transitions polarized along the major axis[22]. These signals caused by the phenanthroline ligands obscure any charge-transfer signals in the 320–340 nm region.

The acidity of protic ligands is markedly increased by coordination to metal ions, and Bennett et al. showed that acidities of chelate ligands are much greater than those of otherwise similar monodentate ligands[23]. A somewhat similar pattern of behavior is observed in the bis(ethylenediamine) complex. The (apparent) pK_a of the mixture of diastereomers of the protonated bis(ethylenediamine) complex **2** is 3.4, a value very similar to that[23] of 3.5 for $[Co(en)_2(HOCH_3CH_2NH_2)]^{3+}$. The p$K_a$ value of glucose is[17] 12.3, and that of the anomeric OH group of glucosamine will be similar. Thus, coordination to Co(III) in the ethylenediamine complex increases acidity by almost nine orders of magnitude. The ammonia complex $[Co(NH_3)_3OH_2 \cdot$ D-glucosamine$]^{3+}$ (**1**), is much less acidic and is not deprotonated in water. Differences in acidity of chelated as opposed to monodentate ligands as already noted[23], and for $[Pt(en)_3]^{4+}$ (pK_a 5.5) and $[Pt(NH_3)_6]^{4+}$ (pK_a 7.9), have been ascribed[24] to differences in solvation. Similar solvation effects could be important in the present complexes, although we are comparing effects of mono- and bi-dentate ligands on the acidity of the anomeric OH group of a bidentate D-glucosamine ligand. To this extent these systems differ from some of those discussed by Bennett et al. In this context it may be noted that α-substituted hydroxy compounds, such as 1,2-diols, are typically more acidic than unsubstituted primary alcohols[23], and HO-1 groups of sugars are relatively acidic, because of the electronic effect of the ring oxygen atom[17].

The bis(phenanthroline) complex (**3**) is less acidic than the bis(ethylenediamine complex) (**2**) and does not deprotonate in water. This observation does not appear to fit a solvation hypothesis[23] because phenanthroline is much bulkier than ethylenediamine. However, phenanthroline is an effective electron donor and it decreases the net charge on Co(III) and the acidity of the HO-1 group of glucosamine that is coordinated to the metal.

Interactions between NH residues of ethylenediamine and the HO-1 residue in the complex should destabilize the conjugate acid of **2**, but hydrogen bonding to the alkoxide residue, directly or through a water molecule, should stabilize **2**. These interactions will be absent in the phenanthroline complex, and in the ammonia complex intramolecular hydrogen-bonding decreases the rotational entropy of the NH_3 ligands. There will be no corresponding loss of rotational entropy in the more-rigid ethylenediamine complex (**2**).

The configurations about Co(III) are established unambiguously from spectral data, but it is more difficult to establish the nature of the linkages between glucosamine and Co(III). Deprotonation of the bis(ethylenediamine) complexes (**2**) strongly suggests that coordination involves the 1 and 2 positions, because the HO-1 group is much more acidic than the other hydroxyl groups[17], although this evidence does not distinguish between coordination of the α rather than the β anomer. The *cis ax, eq* NH_2 and OH or O^- groups in α-glucosamine should favor coordination to Co(III), but this arrangement may cause interference between sugar and the other ligands on cobalt. This interference should be less in complexes of β-glucosamine, which has *trans eq, eq* NH_2 and OH groups. Kozlowski et al. noted that either the HO-1 or -3 group may coordinate to Cu(II) in amino sugars[6]. The higher stability of complexes of mannosides as compared with glucoside or galactoside derivatives suggests that, with the mannose derivatives, coordination involves the *cis*-NH_2 and HO-3 groups. The situation may be different with glucose derivatives, where NH_2 and HO-3 are *trans*-diequatorial.

The Co(III) ammonia and bis(phenanthroline) complexes (**1** and **3**) involve coordination of a hydroxyl group to Co(III). Coordination through the 1-hydroxyl group is postulated for various metal–carbohydrate complexes, but, as noted earlier, coordination through the NH_2-2 and HO-3 group is not excluded[6].

Values of ^1H coupling constants for the Λ isomer of the bis(ethylenediamine) complex (**2**) confirm that coordination is here through the 2-amino and 1-α-alkoxide residues. This evidence is consistent with comparisons of molecular-mechanics simulations and NMR evidence on the structures of this complex, and of the α and β anomers of D-glucosamine as discussed in an accompanying paper.

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