Metal Complexes of Carbohydrates: Isolation and Characterisation of Cobalt(III) Complexes containing *N*-Substituted Glycosylamine Ligands derived from Ethane-1,2-diamine and Glucosamine†

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Reaction between *cis*- or *trans*-$[Co(en)_2Cl_2]^+$ (en = ethane-1,2-diamine) and D-glucosamine (2-amino-2-deoxy-D-glucopyranose) in neutral aqueous solution results in a very complicated product mixture including as a major component several isomeric complex ions in which the co-ordination sphere is formally made up of two ethane-1,2-diamine units and one sugar unit. Separation of these complexes by ion-exchange chromatography, and subsequent spectroscopic and structural studies have shown that they are diastereomeric forms in which the co-ordination sphere actually contains one bidentate ethane-1,2-diamine chelate and a multidentate ligand which is an *N*-(2′-aminoethyl)amino-substituted glycosylamine derived from glucosamine, fructosamine or mannosamine. The presence of the fructosamine moiety reveals that the complex formation reaction is accompanied by the Amadori rearrangement of glucosamine, while the presence of the mannosamine moiety indicates that this rearrangement may be reversible and possibly stereospecific in particular diastereoisomers. Crystal structure determinations have definitively characterised eight of the reaction products as: **1** a complex of the 1-*N*-(2′-aminoethyl)amino-substituted glucosamine in which the sugar, although chelated to the metal as part of a tridentate ligand, is in its open-chain form and in which the four nitrogen atoms derived from the original two ethane-1,2-diamine units are essentially coplanar; **2** a complex of tridentate 1-*N*-(2′-aminoethyl)amino-substituted glucosamine in which the sugar has its pyranose form and the chelate edges spanned by the original ethane-1,2-diamine units are in the Δ configuration; **3** a complex of 1-*N*-(2′-aminoethyl)amino-substituted glucosamine in which the sugar is in its open-chain form and the ligand is bound in a quadridentate manner, with the chelate edges spanned by the original ethane-1,2-diamine units in the Δ configuration; **4** a complex of 1-*N*-(2′-aminoethyl)amino-substituted mannosamine in which the sugar has a furanose form and is part of a quadridentate ligand, and the chelate edges spanned by the original ethane-1,2-diamine units are in the Λ configuration; **5** a complex of quadridentate 1-(2′-aminoethylamino)-1-deoxy-fructopyranosylamine in which the chelate edges spanned by the original ethane-1,2-diamine units are in the Λ configuration; **6** a complex of quadridentate 1-(2′-aminoethylamino)-1-deoxy-fructofuranosylamine in which the chelate edges spanned by the original ethane-1,2-diamine units are in the Δ configuration; **7** the same complex as **6** but in the form where its co-ordinated sugar hydroxyl group is deprotonated; and **8** a complex of 1-(2′-aminoethylamino)-1-deoxyfructopyranosylamine in which the chelate edges spanned by the original ethane-1,2-diamine units are in the Δ configuration.

The ubiquitous natural occurrence of carbohydrates and their affinity for polar media generate a varied and extensive co-ordination chemistry,[1–6] some of which, as in Fehling's and Benedict's tests for reducing sugars,[7] has long been familiar. In general, however, the complexity of carbohydrate-containing systems and the relatively restricted range of techniques which can be applied to the study of the co-ordination of abundant natural cations, such as Na^+ and Ca^{2+},[8] for example, have meant that the development of a detailed understanding of this chemistry has been slow and difficult. As with other important biological molecules such as the amino acids, the possibility of forming complexes with an inert metal ion raises the prospect not only of readily characterising both binding modes and stereochemistry but also of understanding how a given binding mode affects reactivity.[9–11] It is for such reasons that we have been interested in studying the co-ordination of sugars and their derivatives to cobalt(III), even though it was anticipated that this chemistry might be restricted by the reducing properties of many sugars, which could cause at least some complications due to dismutation reactions during synthesis.[12] Exceptionally poor yields of desired species have indeed been reported in some earlier works[13,14] on cobalt(III)–sugar complexes probably in part for this reason. While the chemistry described herein does not provide a means of avoiding difficulties arising from dismutation during synthesis, moderate yields of a number of interesting compounds have been obtained, and we describe their synthesis and stereochemical characterisation as a basis for subsequent reports on their reactivity. The complexes result from the reaction between D-glucosamine and bis(ethane-1,2-diamine)cobalt(III) complexes in neutral aqueous solutions, and have been found to contain derivatives of three sugars, D-glucosamine, D-mannosamine and D-fructosamine. The conditions of synthesis are in fact the same as those described by others[15] as giving rise to good yields of the Δ and Λ diastereoisomers of $[Co(en)_2L]^{2+}$ (en = ethane-1,2-diamine, L = D-glucosamine − H), and an attempt is made here to rationalise these apparently disparate results. In the case of simple sugars, rather than their amino derivatives, it is well known that both epimerisation and isomerisation reactions may be induced in the presence of labile metal-ion amine complexes,[16,17] and there is evidence that such reactions, some

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

of which involve the formation of amino sugars, may be important in a wide variety of biological processes.[18]

Experimental

Reagents and Instrumentation.—Hydrated *cis*- and *trans*-$[Co(en)_2Cl_2]Cl$ salts were prepared by literature methods.[19] D-Glucosamine hydrochloride (Sigma) was used as received. Cation-exchange resins, SP Sephadex (Pharmacia) and Dowex 50W × 2 (Dow Chemical), were used, initially in their Na^+ and H^+ forms, respectively, for chromatography in glass columns under gravity-flow elution. Elemental microanalyses were carried out by MHW Laboratories, Arizona.

Nuclear magnetic resonance spectra were recorded using Bruker AM300 and AMR500 instruments. Electronic absorption spectra were obtained using a Milton-Roy Spectronic 3000 diode array spectrophotometer, and optical rotations were measured on a Perkin-Elmer 141 polarimeter.

Synthesis.—Reaction between $[Co(en)_2Cl_2]^+$ *and* D-*glucosamine.* (The conditions used for this reaction are nearly identical with those of ref. 15 but the treatment of the product mixture differs considerably.) D-Glucosamine hydrochloride (8.62 g) was dissolved in a solution of either *cis*- or *trans*-$[Co(en)_2Cl_2]Cl$ (12.14 g) in water (50 ml; complete dissolution of the *cis* complex resulted only through aquation, so that an extended period of stirring was necessary initially). The pH of this solution was adjusted to a value of 8 by addition of NaOH, and the then deep violet solution was kept at 40 °C for 4 h. After dilution with water (500 ml), the red reaction mixture was absorbed on a column of Dowex 50W × 2 resin (30 × 7 cm) and the column washed well with water. Elution with HCl solutions of gradually increasing concentrations (from 0.5 mol l^{-1}) revealed a large number of components (see Results and Discussion section). Each separate band eluate was evaporated to dryness under reduced pressure and the ^1H NMR spectrum of the residue taken to establish whether or not a sugar was present and, if so, to determine the en : sugar ratio. In this way, it was established that the complexes of interest, those where the ratio was 2 : 1, were eluted relatively easily, and hence the following is an abbreviated description of the complete chromatographic treatment dealing only with these materials. Elution with 0.5 mol l^{-1} HCl rapidly removed a violet band (F1), and exposed red-violet (F2) and red-orange (F3) bands, which were conveniently eluted by increasing the acid concentration to 4 mol l^{-1}. Only F2 and F3 appeared to contain 2 : 1 species. Each was subjected to repeat chromatography on Na^+-form Dowex 50W × 2 resin using 0.5 mol l^{-1} Na_2HPO_4–0.5 mol l^{-1} NaH_2PO_4 solution (known to be effective in the separation of multicomponent reaction mixtures in related systems[20]) as eluent. Band F2 thereby split into three components, F2-1, F2-2 and F2-3 {though the two trailing components were present only in minor amounts which varied in significance in different preparations, and F2-2 was ultimately shown to be largely *cis*-$[Co(en)_2(NH_3)Cl]^{2+}$, so that attempts to characterise the traces of sugar complex with which it appeared to be mixed were abandoned}, the F3 into five components, F3-1 to F3-5. This last component was further split into two, F3-5-1 and F3-5-2, by chromatography on SP Sephadex with 0.05 mol l^{-1} K_2SO_4 as eluent. The cobalt complexes were recovered from these Na^+ or K^+ containing eluates by absorbing the diluted eluates on Dowex 50W × 2, removing the alkali-metal cations by elution with 1 mol l^{-1} HCl, then the cobalt complexes with 4 mol l^{-1} HCl, and evaporating the second eluates to dryness under vacuum. The residues were finally recrystallised from dilute HCl by the addition of ethanol or acetone. Only those from F2-1, F2-3, F3-1, F3-2, F3-3, F3-4 and F3-5-1 appeared to be 2 : 1 en : sugar complexes and for present purposes these are referred to as compounds **1**, **2**, **3**, **4**, **5**, **6** and **8**, respectively. (Compound **7**, obtained during attempts to recrystallise **3** from neutral aqueous solution, proved to be simply a deprotonated form of **6** generated during the time allowed for crystallisation.) Yields of these particular components were 0.46 (2.4), 0.34 (1.9), 0.60 (3.1), 0.80 (4.4), 0.60 (3.1), 0.53 (2.8) and 1.60 g (7.4%), respectively. Specific rotations, measured on aqueous solutions approximately 10^{-3} mol l^{-1}, in a 1 dm cell at 298 K were, respectively: $[\alpha]_{546}$ +470, +58, −485, +628, +382, −1140 and −1186; $[\alpha]_{589}$ −280, +146, +24, +228, −37, −24 and −57 decideg cm^2 g^{-1} (Found for **1**: C, 24.7; H, 6.2; N, 14.8. $C_{10}H_{29}Cl_3CoN_5O_5{\cdot}H_2O$ requires C, 24.90; H, 6.45; N, 14.50; **2**: C, 26.2; H, 6.0; N, 15.0. $C_{10}H_{27}Cl_3CoN_5O_4{\cdot}0.5H_2O$ requires C, 26.35; H, 6.20; N, 15.35; **3**: C, 25.4; H, 6.2; N, 14.1. $C_{10}H_{29}Cl_3CoN_5O_5{\cdot}0.5H_2O$ requires C, 25.35; H, 6.40; N, 14.80; **4**: C, 25.9; H, 5.7; N, 14.3. $C_{10}H_{27}Cl_3CoN_5O_4{\cdot}H_2O$ requires C, 25.85; H, 6.30; N, 15.05; **5**: C, 25.8; H, 6.0; N, 14.4. $C_{10}H_{27}Cl_3CoN_5O_4{\cdot}H_2O$ requires C, 25.85; H, 6.30; N, 15.05; **6**: C, 25.4; H, 6.1; N, 14.6. $C_{10}H_{27}Cl_3CoN_5O_4{\cdot}H_2O$ requires C, 25.85; H, 6.30; N, 15.05; **8**: C, 22.6; H, 6.0; N, 13.0. $C_{10}H_{27}Cl_3CoN_5O_4{\cdot}5H_2O$ requires C, 22.40; H, 6.95; N, 13.05%. These formulations are explained in the Results and Discussion section. Note that these chloride salts all appeared to be weakly deliquescent and hence they were always stored in a desiccator over silica gel.)

Crystals suitable for crystallographic study were obtained as follows: for **1**, crystals of the sulfate were formed by vapour diffusion of acetone into a solution of the chloride in dilute sulfuric acid; for **2**, well developed crystals of the chloride were formed upon vapour diffusion of acetone into a solution of the chloride in dilute HCl; for **3**, crystals of the nitrate were obtained by vapour diffusion of ethanol into a solution of the chloride in dilute nitric acid; for **4** and **5**, crystals of the dithionate salts were formed upon vapour diffusion of ethanol into aqueous solutions of the chlorides to which excess $Li_2S_2O_6$ had been added, and crystals of **7** were obtained when this procedure was applied to **3**; for **6**, crystals of a mixed chloride–bromide were obtained by vapour diffusion of acetone into a solution of the chloride salt in dilute HBr; and for **8**, the chloride crystallised adequately upon vapour diffusion of acetone into a solution of the chloride in dilute HCl. The formulations devised for these crystalline materials on the basis of the models adopted for their structure solutions were: $[Co(en)(C_8H_{21}N_3O_5)Cl]SO_4{\cdot}2H_2O$ **1**, $[Co(en)(C_8H_{19}N_3O_4)Cl]Cl_2{\cdot}ca.\ 0.45H_2O$ **2**, $[Co(en)(C_8H_{21}N_3O_5)][NO_3]_3{\cdot}H_2O$ **3**, $[Co(en)(C_8H_{19}N_3O_4)][S_2O_6]_{1.5}{\cdot}3H_2O$ **4**, $[Co(en)(C_8H_{18}N_3O_4)]S_2O_6{\cdot}2H_2O$ **5**, $[Co(en)(C_8H_{19}N_3O_4)]Cl_{2.68}Br_{0.32}{\cdot}2H_2O$ **6**, $[Co(en)(C_8H_{18}N_3O_4)]S_2O_6{\cdot}H_2O$ **7** and $[Co(en)(C_8H_{19}N_3O_4)]Cl_3{\cdot}5H_2O$ **8**.

Structure Determinations.—(General procedure; individual variations are noted below.) Unique room-temperature diffractometer data sets ($T \approx 295$ K; $2\theta/\theta$ scan mode; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å) were measured, yielding N independent reflections, N_o of these with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\ \sigma^4(I_{diff})$ being used. Neutral-atom complex scattering factors were employed, computation using the XTAL 3.2 program system[21] implemented by S. R. Hall. Pertinent results are given in Fig. 1 and Tables 1–10. Chiralities quoted were established crystallographically in all cases; some stoichiometries quoted are tentative, most particularly in respect of anion and solvent component in consequence of inauspicious or difficult material leading to inferior refinement, and derivative quantities quoted are consistent with the idealised or implied formula given. Hydroxyl hydrogen atoms were established from difference map residues.

Crystal/Refinement data. Complex **1**. $[Co(en)\{H_2N(CH_2)_2NHCH(OH)CH(NH_2)(CHOH)_3CH_2OH\}Cl]SO_4{\cdot}2H_2O$, $C_{10}H_{33}ClCoN_5O_{11}S$, $M = 525.8$, orthorhombic, space group $P2_12_12_1$ (D_2^4, no. 19), $a = 17.82(1)$, $b = 12.15(1)$, $c = 9.07(1)$

Å, U = 1964 Å^3, D_c (Z = 4) = 1.78 g cm^{-3}; F(000) = 1104, μ_{Mo} = 11.6 cm^{-1}; specimen: 0.10 × 0.04 × 0.33 mm; $A^*_{min,max}$ = 1.05, 1.13. $2\theta_{max}$ = 45°; N = 1489, N_o = 786; R, R' = 0.098, 0.115 (preferred chirality); 0.110, 0.117 (alternative hand). The specimen and associated data were inferior; anisotropic thermal parameters were refined for Co and Cl only.

Abnormal features/variations in procedure (≡ *'variata'*). The terminal OH group of the sugar residue was disordered over two sites, populations being set at 0.5 after trial refinement; the associated hydrogen was not located. The anion was initially expected to be chloride but was assigned as sulfate on the basis of the structure solution after recognising that the crystals had actually been obtained from a solution, used for NMR experiments, which had been acidified with D_2SO_4. Artefacts assigned as water molecule oxygens were refined with populations variable; all gave values of ≈1, at which they were constrained.

Complex **2**. [Co(en){$H_2N(CH_2)_2$-NHCHCH(NH$_2$)(CHOH)$_2$CHOCH$_2$OH}Cl]Cl$_2$·*ca* 0.45H$_2$O, $C_{10}H_{27}Cl_3CoN_5O_5$·*ca*. 0.45H$_2$O, M ≈ 454.5, orthorhombic, space group $P2_12_12_1$, a = 19.473(4), b = 13.32(1), c = 7.210(4) Å, U = 1870 Å^3, D_c (Z = 4) = 1.61 g cm^{-3}; F(000) = 946, μ_{Mo} = 13.7 cm^{-1}; specimen: 0.25 × 0.64 × 0.40 mm; $A^*_{min,max}$ = 1.39, 1.72. $2\theta_{max}$ = 65°; N = 3086, N_o = 2463; R, R' = 0.042, 0.047 (preferred chirality); 0.051, 0.056 (alternative hand).

Variata. A difference map artefact was modelled as a water molecule oxygen atom, site occupancy set after refinement at 0.45 without location of associated hydrogen atoms.

Complex **3**. [Co(en){$H_2N(CH_2)_2$NHCH(OH)CH(NH$_2$)-(CHOH)$_3$CH$_2$OH}][NO$_3$]$_3$·H$_2$O, $C_{10}H_{29}CoN_8O_{14}$·H$_2$O, M = 562.4, monoclinic, space group $P2_1$ (C_2^2, no. 4), a = 9.795(5), b = 7.994(3), c = 14.478(2) Å, β = 96.41(1)°, U = 1127 Å^3, D_c (Z = 2) = 1.66 g cm^{-3}; F(000) = 588, μ_{Mo} = 8.5 cm^{-1}; specimen: 0.39 × 0.50 × 0.18 mm: $A^*_{min,max}$ = 1.16, 1.36. $2\theta_{max}$ = 55°; N = 2772, N_o = 2513; R, R' = 0.049, 0.058 (preferred chirality); 0.051, 0.060 (alternative hand).

Complex **4**. [Co(en){$H_2N(CH_2)_2$-NHCHCH(NH$_2$)CH(OH)CHO(CHOH)CH$_2$OH}]-[S$_2$O$_6$]$_{1.5}$·3H$_2$O, $C_{10}H_{33}CoN_5O_{16}S_3$, M = 634.5, tetragonal, space group $P4_32_12$ (D_4^8, no. 96), a = 8.992(2), c = 60.67(2) Å, U = 4830 Å^3, D_c (Z = 8) = 1.74 g cm^3; F(000) = 2648, μ_{Mo} = 10.5 cm^{-1}; specimen: 0.54 × 0.30 × 0.24 mm; $A^*_{min,max}$ = 1.28, 1.41. $2\theta_{max}$ = 50°; N = 2631, N_o = 2119; R, R' = 0.045, 0.054 (preferred chirality); 0.051, 0.059 (alternative hand).

Variata. Intensity standards diminished through the experiment uniformly at ≈8%; data were corrected accordingly. One anion was modelled as disordered about a crystallographic 2 axis S(3,4) being on and off the axis respectively with associated oxygen atoms disposed correspondingly; populations were assigned as 0.5 after trial refinement. Populations of artefacts modelled as lattice water were set at 1 or 0.5 after trial refinement and considerations of their disposition *vis-a-vis* the disordered anion components. Data were obtained by a ω-scan because of the long c axis.

Complex **5**. [Co(en){$H_2N(CH_2)_2$NHCH$_2$-C(NH$_2$)CHO(CHOH)$_2$CH$_2$O}]S$_2$O$_6$·2H$_2$O, $C_{10}H_{30}CoN_5S_2O_{12}$, M = 535.5, monoclinic, space group $P2_1$, a = 10.038(1), b = 10.054(4), c = 10.217(2) Å, β = 93.44(1)°, U = 1029 Å^3, D_c (Z = 2) = 1.73 g cm^{-3}; F(000) = 560, μ_{Mo} = 11.1 cm^{-1}; specimen: 0.21 × 0.50 × 0.09 mm; $A^*_{min,max}$ = 1.10, 1.25. $2\theta_{max}$ = 65°; N = 3415, N_o = 2663; R, R' = 0.041, 0.039 (preferred chirality); 0.044, 0.043 (alternative hand).

Complex **6**. [Co(en){$H_2N(CH_2)_2$NHCH$_2$-C(NH$_2$)(CHOH)$_2$CHOCH$_2$OH}]Cl$_{2.68}$Br$_{0.32}$·2H$_2$O, $C_{10}H_{31}Br_{0.32}Cl_{2.68}CoN_5O_6$, M = 496.9, orthorhombic, space group $P2_12_12_1$, a = 22.989(7), b = 11.534(4), c = 7.533(3) Å, U = 1997 Å^3, D_c (Z = 4) = 1.65 g cm^{-3}; F(000) ≈ 1031, μ_{Mo} ≈ 18.9 cm^{-1}; specimen: 0.18 × 0.11 × 0.32 mm; $A^*_{min,max}$ = 1.22, 1.39. $2\theta_{max}$ = 55°; N = 2031, N_o = 1294; R, R' = 0.053, 0.052 (preferred chirality); 0.058, 0.056 (alternative hand).

Variata. The CH$_2$OH oxygen of the sugar residue was modelled as disordered over two sites, set at equal occupancy after trial refinement. With all anion residues modelled as Cl, R was 0.063; refinement of halogen components as Cl/Br with a total of 1 at any site resulted in the distributions given for anions 1, 2. Residues modelled as lattice water were held at population 1 after trial refinement.

Complex **7**. [Co(en){$H_2N(CH_2)_2$NHCH$_2$-C(NH$_2$)(CHO)CHOHCHOCH$_2$OH}]S$_2$O$_6$·H$_2$O, $C_{10}H_{28}CoN_5O_{11}S_2$, M = 517.4, monoclinic, space group $P2_1$, a = 7.625(2), b = 12.162(9), c = 10.14(1) Å, β = 97.42(6)°, U = 932 Å^3, D_c (Z = 4) = 1.84 g cm^{-3}; F(000) = 540, μ_{Mo} = 12.1 cm^{-1}; specimen: 0.24 × 0.16 × 0.27 mm; $A_{min,max}$ = 1.21, 1.34. $2\theta_{max}$ = 60°; N = 2652, N_o = 2286; R, R' = 0.045, 0.049 (preferred chirality); 0.048, 0.053 (alternative hand).

Variata. A difference map artefact was assigned as lattice water; after trial refinement, its population was set at 1. All hydrogen atoms were located in difference maps, no substantial residues being found in association with O(2).

Complex **8**. [Co(en){$H_2N(CH_2)_2$NHCH$_2$-C(NH$_2$)(CHOH)$_3$CH$_2$O}]Cl$_3$·5H$_2$O, $C_{10}H_{37}Cl_3CoN_5O_9$, M = 536.7, orthorhombic, space group $P2_12_12_1$, a = 14.695(8), b = 12.746(3), c = 12.053(2) Å, U = 2258 Å^3, D_c (Z = 4) = 1.58 g cm^{-3}; F(000) = 1128, μ_{Mo} = 11.6 cm^{-1}; specimen: 0.63 × 0.19 × 0.19 mm; $A^*_{min,max}$ = 1.20, 1.33. $2\theta_{max}$ = 60°; N = 3671, N_o = 3008; R, R' = 0.036, 0.036 (preferred chirality); 0.046, 0.046 (alternative hand).

Variata. Difference map artefacts were modelled as lattice water O(5), disordered between locations O(05) and O(06), refined with a total population constrained to unity. Hydrogen atoms on the minor component O(6) were not located, but all others were refined.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Only a partial description of the chromatographic treatment of the reaction mixture has been given in the Experimental section since this is sufficient to define procedures necessary for the isolation of all species which result from the binding of one monosaccharide and two ethane-1,2-diamine moieties to one cobalt(III). However, it is important to recognise that several other reaction products are present, since this has a bearing on the analysis of reactions occurring during the synthesis. Thus, spectroscopic measurements on the complexes present in all bands observed to be eluted from Dowex 50W × 2 by HCl show the presence of some free Co^{II}, some free glucosamine (perhaps bound to Co^{II} in the actual reaction mixture), possibly some Co^{III} species with two bound sugar ligands, and some [Co(en)$_3$]$^{3+}$. These are indicators of dismutation catalysed by Co^{II} formed in a redox reaction between the Co^{III} and D-glucosamine reactants, such dismutation being a long-known feature of closely related syntheses.[12,22] Thus, although *cis*- and *trans*-[Co(en)$_2$(OH$_2$)(OH)]$^{2+}$[23] may be the principal cobalt-containing reactants initially present and their lability may be an important factor determining the overall reaction period, some reduction to the very much more labile Co^{II} must occur to explain the transfer of ethane-1,2-diamine ligands between cobalt centres. If this results in appreciable concentration of 'free' ethane-1,2-diamine, the possibility of its reaction with glucosamine also complicates analysis of the synthesis. It should also be noted that the product distribution presently described is kinetically determined and the 4 h reaction period defined is simply one where yields of the variety of products are sufficient to allow relatively facile characterisation of each material.

The composition of solutions of reducing sugars such as D-glucosamine can be extraordinarily complicated,[24] so that there are good reasons to anticipate the formation of a number of isomeric complex ions in the presence of a metal ion, even though one of the well established uses of transition-metal ions such as Cu^{II} is to simplify the characterisation of sugars.[25,26] In the present study, the likely chirality of the disposition of chelate rings about Co and the presence of co-ligands (ethane-1,2-diamine) known to form sugar derivatives directly add further dimensions to the consideration of complex formation by an ambidentate ligand with several possible configurations and conformations. For all these reasons, we felt it imperative to carry out a detailed structural characterisation of any crystalline complex, and the results we have obtained have indeed defined a remarkably complicated series of reactions.

The individual crystals of all substances subjected to room temperature, single-crystal structure determinations were assigned unambiguously to chiral space groups with one formula unit as the asymmetric unit of the structure, with one chiral setting giving a significantly lower residual than the other, thus establishing putative absolute configurations. This led to configurations at the various carbon centres of the sugar units completely consistent with their expected membership of the D series (explained in detail later). Fig. 1 shows the eight cations in the configurations found. Complexes **1**, **2** and **3** contain various forms of glucosamine, whereas complexes **4**–**8** contain amino sugars derived from reactions at C^1 and C^2 of glucosamine. In all, the sugar unit has been linked to one of the two ethane-1,2-diamine ligands present in the reactant complex. In some cases, disorder is observed among lattice residues (anions, solvent); although this may affect the precision of the determination adversely in these cases, the principal features of interest within the complex cations remain clearly established and useful at the level desired.

Although the determination of the crystal structure of the sulfate salt **1** is less than desirably precise, and is perhaps most affected by the difficulties just mentioned, it suffices to establish unambiguously ring and ligand conformations, connectivity and stereochemistry throughout the cation. The primary, N_5Cl co-ordination sphere of the Co^{III} derives from a unidentate chloride ligand, a bidentate ethane-1,2-diamine ligand and a tridentate (N_3) ligand which is a facially bound 1-*N*-(-2′-aminoethyl)amino-substituted glucosamine in open-chain form. The four nitrogen donor atoms which can be considered to derive from the original two ethanediamine ligands are essentially coplanar, *i.e.*, the chloride and the sugar amino group donor atoms are *trans*. The true ethanediamine chelate ring has the δ conformation, as does the ring of the ethanediamine unit bound to the sugar. The chelate ring involving the sugar C^1 and C^2 atoms has the λ conformation and the hydroxyl group on C^1 is axial, while the nitrogen groups are necessarily *gauche*. Along the open sugar chain, the 2-amino and 3-hydroxy, and the 3- and 4-hydroxy substituents are also in *gauche* orientations but the 4- and 5-hydroxy groups are *trans* while the 6-hydroxy group is disordered over two positions *gauche* and *trans* to the 5-hydroxy group. The carbon-atom configurations at positions 2, 3, 4 and 5 are *R*, *R*, *S* and *R*, respectively, as expected for D-glucosamine.[27]

In the cation of the chloride salt **2**, the primary co-ordination sphere is made up of the same donor atoms as in **1**, again derived from unidentate, bidentate and facial tridentate ligands with the same chelate ring conformations as in **1**. The chelate edges spanned by the two ethanediamine residues, however, here adopt a Δ-*cis* configuration and the sugar, D-glucosamine, is present in its pyranose ring form, with 1-*N* nitrogen as an equatorial (β) substituent.

In the cation of the nitrate salt **3**, the same ligands are found as in the cation of **1** except that the chloride ligand has been displaced by the 3-hydroxyl group of the glucosamine moiety, necessitating rearrangement of the cobalt co-ordination sphere to accommodate the sugar derivative in a quadridentate form such that the chelate edges spanned by the two ethanediamine residues adopt a Δ-*cis* configuration. The true ethanediamine chelate ring has the λ conformation, while the ethanediamine unit bound to the sugar is in the δ conformation. The hydroxyl group on C^1 of the sugar is axial on the chelate ring involving N(2) and N(21), as is C(3), presumably as a result of the co-ordination of O(3) to the cobalt. Oxygen O(4) is *gauche* to O(3) and *trans* to O(5), which is *gauche* to O(6). In the cation of the dithionate salt **4**, the N_5O co-ordination sphere of the Co^{III} derives from two neutral ligands, one an ethanediamine chelate and the other a quadridentate form of a 1-*N*-(2′-aminoethyl)-amino-substituted mannosamine in the furanose form, *i.e.* relative to the reactant D-glucosamine, the sugar unit in **4** has been obtained by inversion of configuration at C^2. The 3-hydroxyl, 2-amino and 1-*N*-(2′-aminoethyl)amino groups of the sugar form a tripod binding unit on one octahedral face about Co^{III} and are all substituents of the approximately envelope-form furanose ring of the sugar. The 5-hydroxy group is *trans* to the ring ether oxygen and *gauche* to the 6-hydroxy group. The isolated ethanediamine chelate ring has the δ conformation while the ethanediamine residue of the glycoside, which takes the Λ configuration relative to the ethanediamine chelate edge, has the λ conformation.

The immediate cation environment in the dithionate salt **5** is very similar to that in **4** except that the co-ordinated sugar hydroxyl group is deprotonated. The ethanediamine chelate again has the δ conformation, although somewhat flattened relative to that in **4**, and the ethanediamine residue of the uninegative quadridentate ligand has the λ conformation, as well as spanning a chelate edge which is in the Λ configuration relative to the chelate edge spanned by the bidentate ligand. A very significant structural difference from **4** is, however, that the quadridentate ligand contains a fructose residue in its pyranose form, the ligand being 1-(2′-aminoethylamino)-1-deoxy-fructo-pyranosylamine. The 2-amino and 3-hydroxy groups are equatorially disposed on the pyranose ring, while C^1 and the 5-hydroxy group are axial. Thus, ignoring the deprotonation of the 3-hydroxy group, **5** is simply an isomer of **4** produced by an aldose to ketose rearrangement without change in the primary co-ordination sphere of the metal. Such an interconversion and the overall conversion of glucosamine to fructosamine it implies can be regarded as particular examples of the Amadori rearrangement,[18,28] which is usually observed as an acid-catalysed reaction of sugars in the presence of amines, presuming that here the Lewis acid Co^{3+} takes over the usual role of H^+ (see below).

The cation present in the mixed chloride–bromide salt **6** is very similar to that in **5** in that again the ligands present are an ethanediamine chelate and a quadridentate *N*-(2-aminoethyl) derivative of the carbinolamine of fructosamine, this time in a neutral form. However, there are two very significant differences in that the ethanediamine residues are now in a Δ relative configuration and the sugar in a furanose form. This inversion of the *cis*-$Co(en)_2$ unit is accompanied by inversion of the true ethanediamine chelate ring conformation to λ and of the sugar derivative ethanediamine ring conformation to δ. The sugar ring is puckered, and the 6-hydroxy group is disordered over two sites *gauche* and *trans* to the C^5 hydrogen.

The dithionate salt **7**, obtained during attempts to crystallise the complex present in **3** from neutral solutions, contains a cation which is simply the 3-hydroxyl deprotonated form of that in **6**. Removal of the co-ordinated hydroxyl proton appears to result in very slight structural changes aside from the fact that the 6-hydroxy group is no longer disordered over two sites and now is found only *gauche* to the C^5 hydrogen.

The complex cation found within the crystal lattice of the chloride salt **8** is very similar to that in **6** (and **7**) in regard to the configuration about Co^{III} and the presence of a quadridentate ligand derived from fructosamine but it is probably better considered as related to **5** by a simple inversion about cobalt, since the ligand is 1-(2′-aminoethylamino)-1-deoxy-fructo-

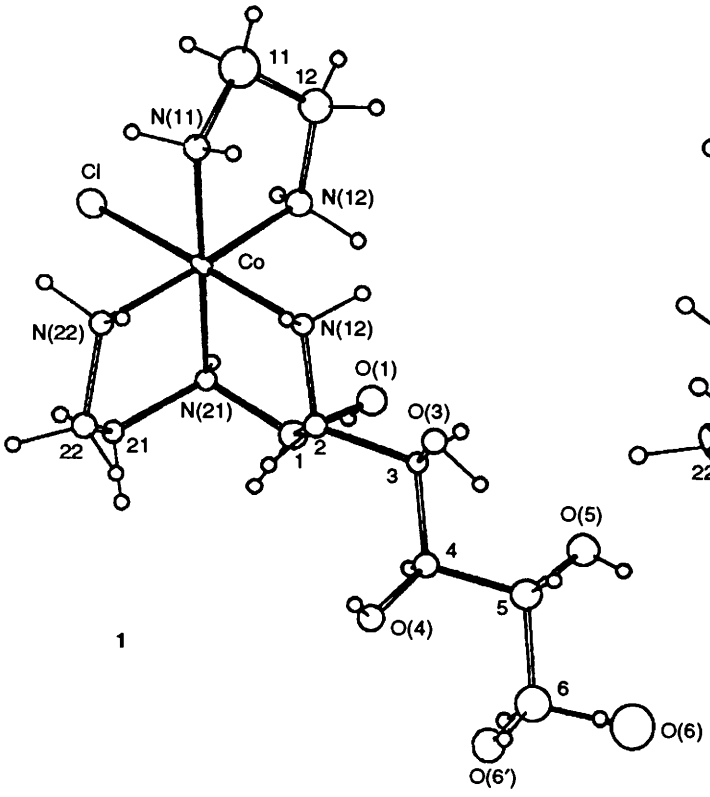
pyranosylamine again. One face of the co-ordination octahedron is occupied by the two nitrogen atoms and the 3-hydroxyl group oxygen of the 1-aminofructosylamine moiety of this quadridentate ligand, and the pendant aminoethyl arm spans an edge which is in a Δ orientation with respect to the chelate edge spanned by the ethanediamine ligand, which is bound in a λ conformation whereas the pendant arm chelate has a δ conformation. The 2-amino and 5-hydroxy substituents of the pyranose ring are axially disposed, with the epimeric (2) carbon having the *R* configuration and the 3, 4 and 5 carbons having, respectively, the *S*, *R* and *R* configurations expected for retention of those of D-glucosamine (where the designations are *R*, *S* and *R*, respectively).[27]

Bond lengths and bond angles within the complex ions (Table 1) do not appear to be unusual. The Co–N and Co–O distances lie within the range seen in many related complexes,[29,30] (although significant variations are found, notably in situations such as that offered by complex **7**, where a deprotonated hydroxyl ligand is present) and some distortions of the co-ordination sphere from true octahedral geometry are expected given the asymmetric ligand environment. Five-membered chelate ring donor atom–Co–donor atom bond angles for the octahedral face spanned by the 1-aminofructosylamine moiety are small but a similar contraction has been observed in the cage complex $[CoL][NO_3]_3$ (L = 1-chloro-8-chloromethyl-3,6,10,13,16,19-hexaazabicyclo[6.6.5]nonadecane),[29] where an octahedral face spanned by a similar chelate ring structure is present. Geometry within the sugar pyranose rings is similar to that found in both D-glucosamine hydrochloride[31] and fructose,[32] indicating that co-ordination engenders no significant additional strain. Torsion angles within all the sugar units presently characterised are given in Table 2.

The conversion of glucosamine to fructosamine involves changes which are very readily detected by both ^1H and ^{13}C NMR spectroscopic measurements. Thus, the observation of two methylene carbon resonances (in addition to those ascribable to ethane-1,2-diamine) in the ^{13}C NMR spectra of some of the present materials was the first clear evidence that not all were complexes of glucosamine derivatives. The complete asymmetry of the complex ions is reflected in the fact that the ^{13}C NMR spectra of compounds **1**–**8** (Table 3) all show ten distinct resonances, and DEPT (distortionless enhancement by polarisation transfer) editing shows clearly that compounds **5**, **6** (≡**7**) and **8** each contain two methylene carbons whereas **1**, **2**, **3** and **4** each contain only one, indicating that the first group is one of ketosamine derivatives, the second of aldosamine. In other work,[13,14] it has been stated that the formation of a co-ordinated ethane-1,2-diamine glycosylamine of an aldose is associated with a marked downfield shift (≈6 ppm) of the resonance of the ethanediamine carbon directly bound to the glycosylated nitrogen. The generality of this conclusion is not apparent from our results, although it is not certain in all cases which methylene carbon resonance should be assigned to an ethanediamine moiety rather than the sugar. Both ^1H and ^{13}C NMR spectra have been useful in confirming the structures revealed by X-ray crystallography but because of signal overlap in the ^1H NMR spectra, we have not been successful in conducting a full analysis of sugar proton coupling constants to assess solution conformations independently.

The very complicated nature of the product mixture from the reaction between bis(ethane-1,2-diamine)cobalt(III) complexes and D-glucosamine that we have observed is surprising in view of the literature report on this system indicating that only Δ- and Λ-diastereoisomers of $[Co(en)_2L]^{2+}$ (L = D-glucosamine − H) should be present,[15] especially given that the actual preparative conditions were essentially identical (and indeed ours were based on those given in ref. 15). One reason for the differences may be the much more extensive chromatographic treatment, often requiring up to 2 d for completion, that we have employed. Given our observations that nearly all the pure species we have isolated undergo quite rapid reactions in base (carbonate solutions of pH ≈ 10), it is possible that some such reaction occurs in the pH ≈ 7 phosphate buffers used for elution of the mixtures of complexes from SP Sephadex cation-exchange resin, so that the materials we have finally isolated are not the immediate reaction products but have been formed during the chromatography. Inconsistent with this, however, is the observation that the various complexes we have isolated are single species. Much more reasonable, therefore, would seem to be the proposition, based on acceptance of our observations that co-ordinated D-glucosamine is rather reactive in basic solutions, that the particular product distribution obtained may be very sensitive to both pH and temperature control during the reaction period, as well as to the exact length of that period (and certainly we have shown, as noted previously, that the product distribution is kinetically determined). We have attempted to reproduce the exact procedure of ref. 15 but there is a difficulty in that the conditions used in evaporation of the 'final' reaction mixture are not precisely specified, and hence we have carried this out at the lowest possible temperature (≈20 °C) in the belief that this would minimise any further transformations. Under these conditions, SP Sephadex/K_2SO_4 chromatography of the reaction product gave a distribution of bands superficially similar to that described in ref. 15 but only the second of our bands contained co-ordinated sugars and it was still very obviously (^{13}C NMR) a mixture (with at least six components being detected on repeat chromatography using SP Sephadex and phosphate buffer eluent). Hence, we are unable to explain definitively the disparities between our and the earlier results, although the structural results we have obtained lead us to the conclusion that spectroscopic methods (circular dichroism, NMR spectroscopy, in particular) alone are inadequate for the characterisation of species present in such constitutionally and stereochemically complicated systems. It is noteworthy that in repeating our preparative procedure many times, there have been occasions when, in addition to the complexes described above, trace amounts of compounds which we have only been able to prepare in good yields by treatment of some of the isolated complexes with base, have been detected. Some of these appear to be aldimine species, as indicated by the presence of low-field (δ ≈9) CH resonances in their ^1H NMR spectra, and they may well be important intermediates in the various interconversions defined by the present structural studies, so that we are currently investigating their chemistry in detail.

Chemically, the two most significant features of the present structure determinations are the demonstration of the facile interconversion of at least three sugars under the preparative conditions and the indication of the importance of *N*-substituted glycosylamines in these reactions. The conversion of co-ordinated glucosamine to fructosamine and mannosamine, possibly *via* enediamine formation and isomerisation (Fig. 2), is, as noted previously, an example of a well known sugar rearrangement,[18,28] although the detailed mechanism of the occurrence of the Amadori and similar reactions under metal-ion catalysis or promotion is poorly understood,[16,17] and an extension of the present work will involve an extended kinetic study of this process. That the co-ordinated fructosamine product is actually present as a 1-aminofructosylamine indicates that the rearrangement occurs on Co^{III}, since in the normal Amadori reaction the (presumed) imine initial product undergoes hydrolysis to the carbonyl compound or its hydrate. The chelate effect and the inert nature of the Co^{III}–N bond should both retard hydrolysis in the bound species. If the rearrangement occurs on Co^{III}, then the reactant species must be the complex of the *N*-substituted glycosylamine formed from D-glucosamine and ethane-1,2-diamine, showing that the first step in the present syntheses must be very similar to that occurring in the syntheses of Co^{III} complexes of the *N*-(2-aminoethyl)-substituted glycosylamines of mannose, rhamnose and ribose[13,14] and of the structurally characterised Ni^{II} complexes of similar glycosylamines of galactosamine, glucosamine and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Cl
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Co
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N(12)
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O(3)
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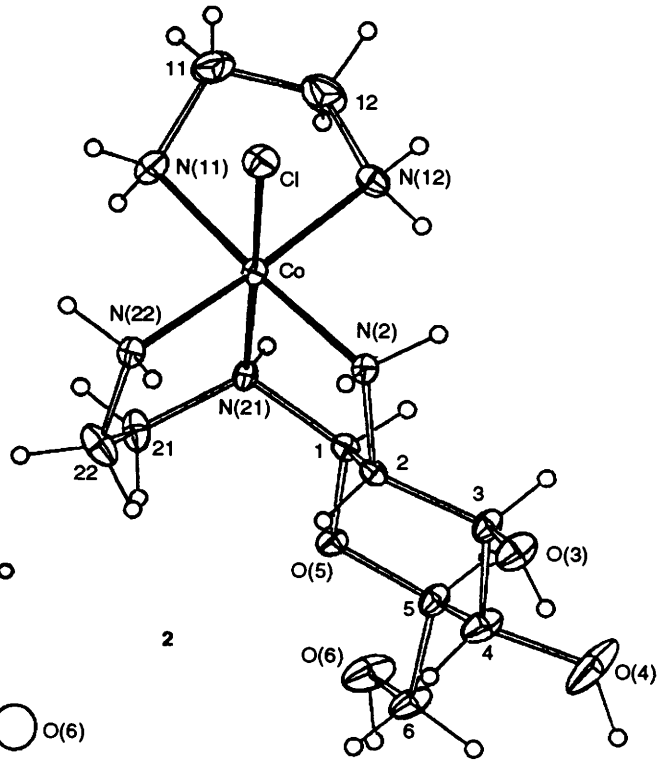
1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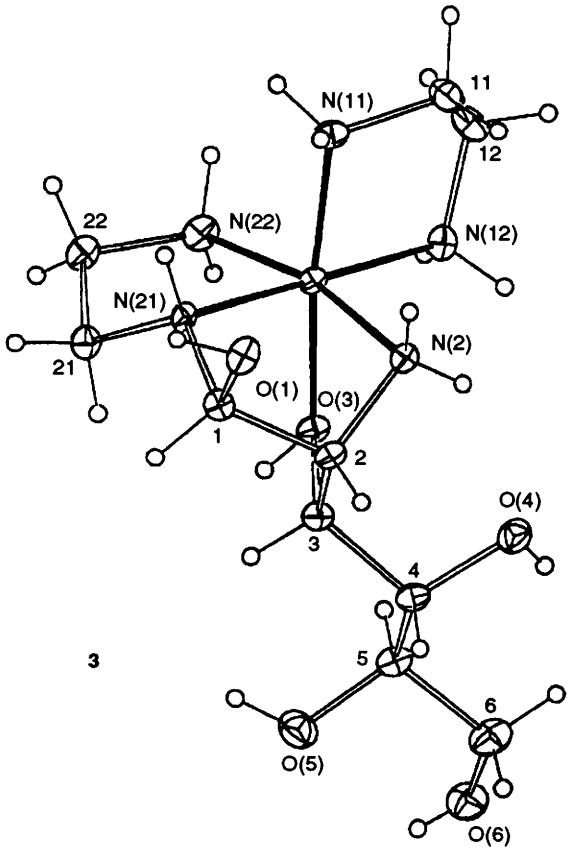
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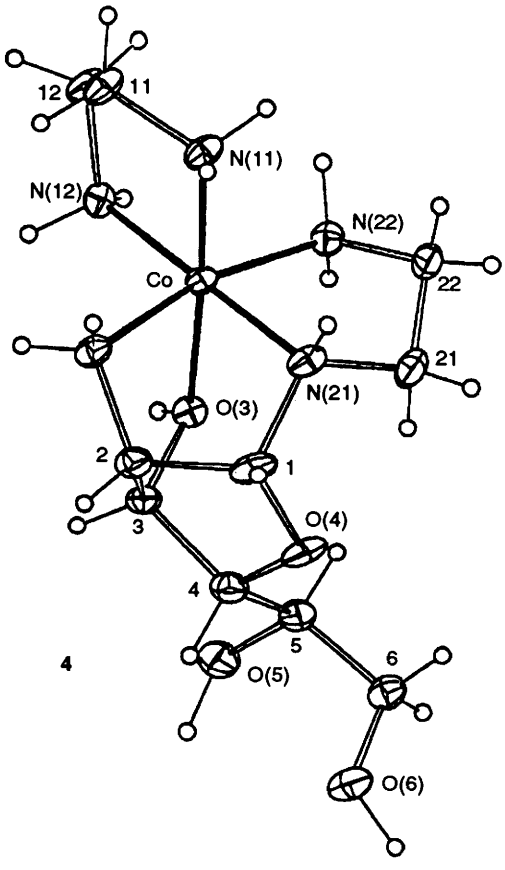
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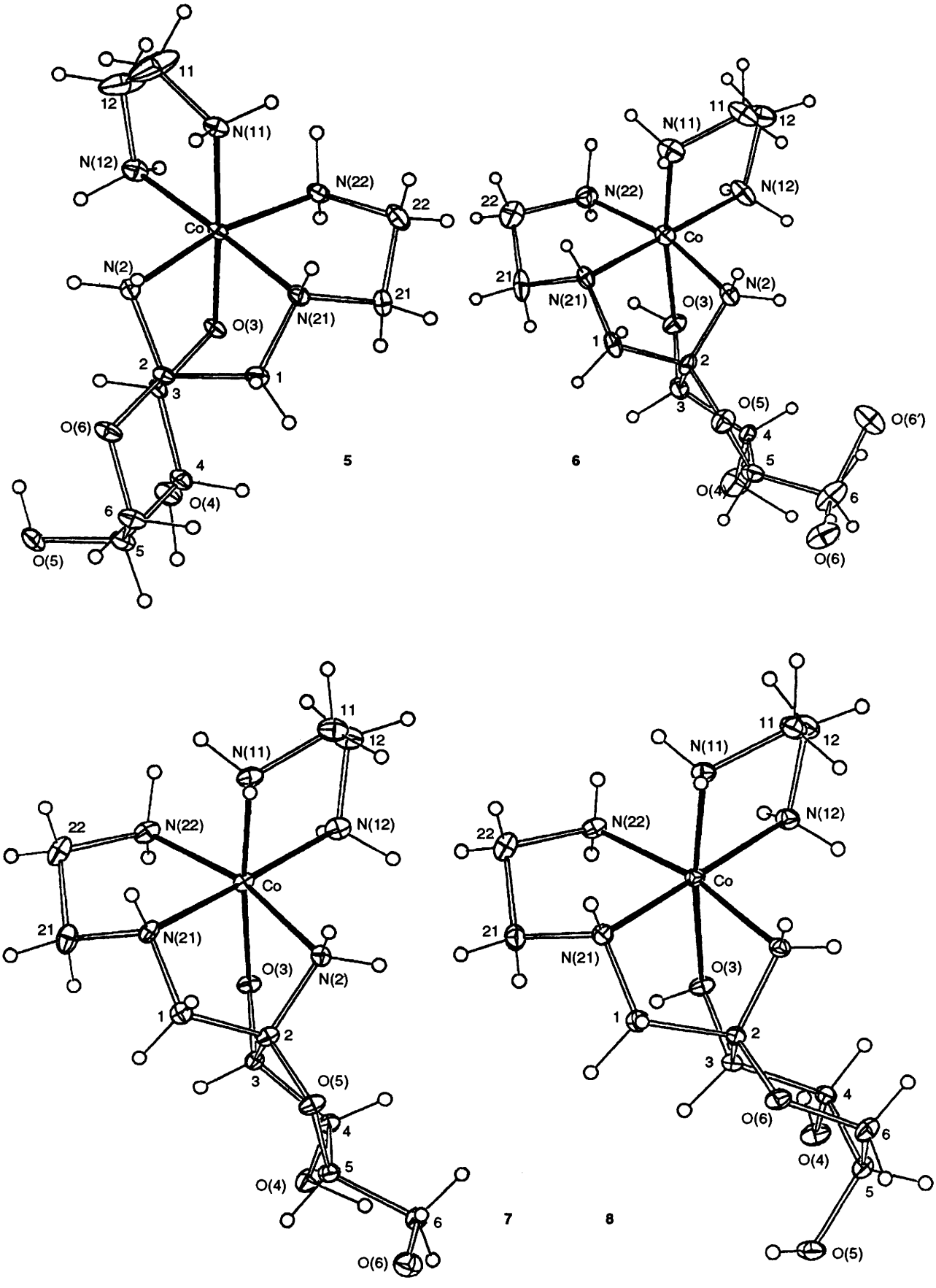

Fig. 1 Projections of the cations of **1**–**8**; 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms are shown with an arbitrary radius of 0.1 Å

Table 1 Cation core geometries, **1–8**

Caveat—Torsion angles are all referenced for a Δ setting of the cobalt environment for comparability; actual values for **4** and **5** are of opposite sign to those given.

(*a*) Compounds **1** and **2** [X is *trans* to N(2), being Cl in **1**; N(11) in **2**; Y is *trans* to N(21), being N(11) in **1** and Cl in **2**]

	1	**2**
Distances/Å		
Co–X	2.25(1)	1.967(5)
Co–Y	1.94(3)	2.258(2)
Co–N(12)	1.96(3)	1.959(4)
Co–N(2)	1.92(3)	1.968(4)
Co–N(21)	1.94(3)	1.958(4)
Co–N(22)	1.96(3)	1.966(4)
Angles/°		
X–Co–Y	90(1)	91.7(1)
X–Co–N(12)	87.6(9)	84.9(2)
X–Co–N(2)	174.6(8)	176.5(2)
X–Co–N(21)	90.3(9)	91.8(2)
X–Co–N(22)	89.6(8)	91.8(2)
Y–Co–N(12)	88(1)	89.8(1)
Y–Co–N(2)	95(1)	89.3(1)
Y–Co–N(21)	179(1)	174.1(1)
Y–Co–N(22)	92(1)	89.6(1)
N(12)–Co–N(2)	90(1)	91.8(2)
N(12)–Co–N(21)	92(1)	95.2(2)
N(12)–Co–N(22)	177(1)	176.6(2)
N(2)–Co–N(21)	85(1)	87.4(2)
N(2)–Co–N(22)	92(1)	91.5(2)
N(21)–Co–N(22)	88(1)	85.6(2)
Torsion angles/°		
Co–N(11)–C(11)–C(12)	−36(5)	34.8(7)
N(11)–C(11)–C(12)–N(12)	41(6)	−38.6(8)
C(11)–C(12)–N(12)–Co	−25(5)	24.0(7)
Co–N(2)–C(2)–C(1)	33(3)	29.6(4)
N(2)–C(2)–C(1)–N(21)	−43(3)	−45.1(5)
C(2)–C(1)–N(21)–Co	36(3)	38.2(4)
C(2)–C(1)–N(21)–C(21)	−83(3)	−84.3(5)
C(1)–N(21)–C(21)–C(22)	82(3)	87.3(6)
Co–N(21)–C(21)–C(22)	−39(3)	−33.8(5)
N(21)–C(21)–C(22)–N(22)	42(4)	35.8(6)
C(21)–C(22)–N(22)–Co	−25(3)	−21.1(6)

(*b*) Compounds **3–8**

	3	**4**	**5**	**6**	**7**	**8**
Distances/Å						
Co–N(11)	1.928(5)	1.925(7)	1.986(4)	1.93(1)	1.971(6)	1.929(3)
Co–N(12)	1.948(5)	1.956(6)	1.957(4)	1.93(1)	1.963(6)	1.963(3)
Co–N(21)	1.939(5)	1.941(6)	1.946(4)	1.96(1)	1.947(5)	1.946(3)
Co–N(22)	1.963(6)	1.945(7)	1.941(4)	1.93(1)	1.965(5)	1.946(4)
Co–O(3)	1.935(4)	1.937(5)	1.908(3)	1.979(8)	1.914(4)	1.968(3)
Co–N(2)	1.949(5)	1.938(7)	1.965(4)	1.93(1)	1.953(5)	1.954(3)
Angles/°						
N(11)–Co–N(12)	85.9(2)	85.9(3)	85.4(2)	85.5(4)	85.2(2)	85.9(1)
N(11)–Co–N(21)	93.5(2)	94.5(3)	96.3(2)	93.2(4)	91.9(2)	93.7(1)
N(11)–Co–N(22)	95.2(2)	95.1(3)	91.9(2)	93.5(5)	92.1(2)	93.9(2)
N(11)–Co–O(3)	173.8(2)	176.0(3)	176.9(2)	172.2(4)	174.6(2)	173.4(1)
N(11)–Co–N(2)	95.1(2)	93.1(3)	93.5(2)	96.2(4)	96.5(2)	92.8(1)
N(12)–Co–N(21)	179.3(2)	179.2(3)	178.2(2)	178.7(4)	177.1(2)	179.4(1)
N(12)–Co–N(22)	93.9(2)	92.3(3)	92.8(2)	94.1(5)	94.3(2)	92.8(2)
N(12)–Co–O(3)	90.4(2)	93.1(2)	91.5(2)	88.9(4)	89.9(2)	90.1(1)
N(12)–Co–N(2)	94.4(4)	96.5(2)	97.9(2)	96.0(5)	96.2(2)	97.5(1)
N(21)–Co–N(22)	85.8(2)	87.0(3)	87.2(2)	86.1(4)	86.2(2)	86.8(1)
N(21)–Co–O(3)	90.2(2)	86.5(2)	86.9(2)	92.4(4)	93.0(2)	90.3(1)
N(21)–Co–N(2)	85.9(2)	84.1(3)	82.0(2)	84.0(4)	83.7(2)	82.9(1)
N(22)–Co–O(3)	90.0(2)	88.8(2)	88.5(2)	92.4(4)	90.5(2)	91.5(1)
N(22)–Co–N(2)	167.1(2)	168.3(3)	168.4(2)	166.6(4)	166.9(2)	168.1(1)
O(3)–Co–N(2)	80.2(2)	83.1(7)	86.7(1)	79.0(4)	81.8(2)	82.5(1)

Table 1 (*contd*)

	3	4	5	6	7	8
Torsion angles /°						
Co–N(11)–C(11)–C(12)	43.5(6)	43.3(8)	10.5(8)	41(1)	38.1(6)	44.3(4)
N(11)–C(11)–C(12)–N(12)	−50.5(7)	−47.5(9)	−15.0(8)	−44(2)	−49.1(7)	−48.9(5)
C(11)–C(12)–N(12)–Co	34.5(6)	30.9(8)	11.5(8)	28(1)	37.0(6)	31.4(4)
Co–N(22)–C(22)–C(21)	−22.5(7)	−40.1(8)	−38.0(5)	−28(1)	−32.0(6)	−33.7(4)
N(22)–C(22)–C(21)–N(21)	44.3(7)	51.8(9)	53.2(5)	49(1)	51.2(7)	49.4(4)
C(22)–C(21)–N(21)–Co	−45.8(6)	−38.5(8)	−42.8(5)	−47(1)	−46.6(6)	−41.8(4)
C(22)–C(21)–N(21)–C(1)	−168.3(5)	−161.4(7)	−163.5(4)	−171(1)	−171.7(5)	−165.1(3)
C(21)–N(21)–C(1)–C(2)	105.8(5)	130.6(7)	124.8(4)	109(1)	111.2(6)	122.9(4)
Co–N(21)–C(1)–C(2)	−16.0(5)	8.2(8)	4.4(4)	−13(1)	−12.3(5)	0.3(4)
N(21)–C(1)–C(2)–N(2)	51.4(6)	30.3(9)	38.3(4)	49(1)	50.4(6)	38.6(4)
N(21)–C(1)–C(2)–C(3)	−65.6(6)	−85.5(7)	−74.8(5)	−67(1)	−65.5(6)	−76.4(4)
N(21)–C(1)–C(2)–O(*n*)	—	—	157.0(3)	173(1)	173.8(5)	160.5(3)
Co–O(3)–C(3)–C(2)	−3.7(5)	7.0(7)	30.0(4)	−8(1)	−8.2(5)	8.3(3)
O(3)–C(3)–C(2)–C(1)	78.2(5)	74.9(7)	52.8(5)	81(1)	82.5(6)	69.3(4)
O(3)–C(3)–C(2)–N(2)	−37.2(6)	−42.4(8)	−61.8(4)	−32(1)	−33.1(6)	−44.6(4)
O(3)–C(3)–C(2)–O(*n*)	—	—	−179.3(3)	−154(1)	−153.8(5)	−170.9(3)
Co–N(2)–C(2)–C(1)	−60.9(4)	−53.7(7)	−60.8(3)	−61(2)	−63.5(4)	−58.4(3)
Co–N(2)–C(2)–C(3)	60.3(5)	56.6(7)	59.3(3)	59(1)	56.2(4)	59.0(3)
Co–N(2)–C(2)–O(*n*)	—	—	178.8(3)	176(1)	173.3(4)	−175.6(2)

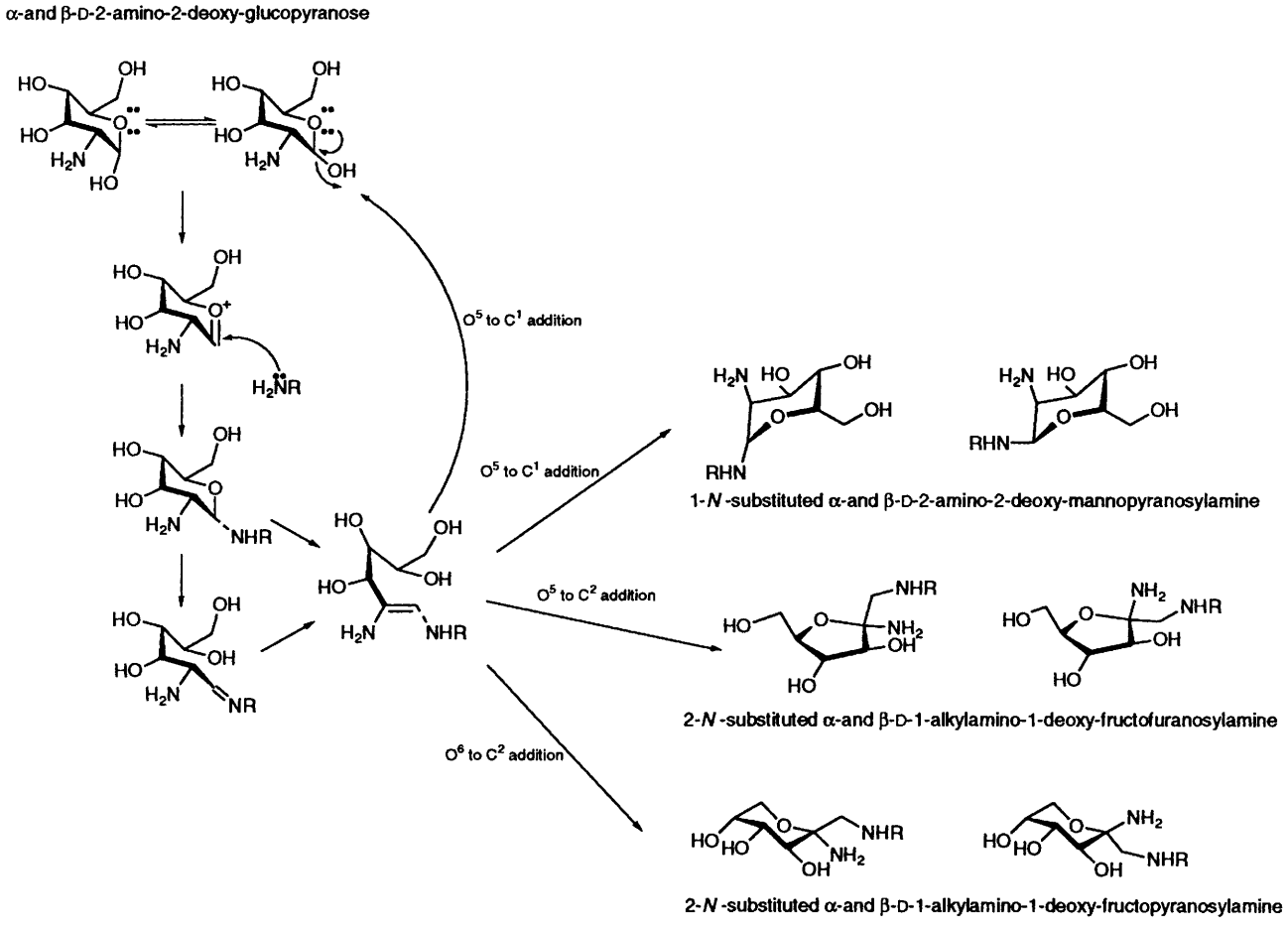

Fig. 2 Sugar interconversion reactions through *N*-substituted glycosylamine formation (the Amadori reaction[28])

mannosamine.[4,35–37] It would be expected that the intramolecular cyclisation of an *N*-bound 2-aminocarbonyl compound to give an amino–imine or amino–carbinolamine chelate would be rapid under the conditions presently used for synthesis of the sugar complexes,[38] so that provided a unidentate *N*-bound amino sugar were in rapid equilibrium with its open-chain carbonyl form, compounds **1** and **2** could be regarded as the most likely initially observable products of the reaction between D-glucosamine and $[Co(en)_2Cl_2]^+$. Assuming the very first reaction step to be like that with simple amines and to involve co-ordination of the D-glucosamine 2-amino group to cobalt and also that the sugar would be in its pyranose form at this stage, the possibilities for any reaction other than glycosylamine formation (ignoring those such as Co–Cl hydrolysis and rearrangement of the donor atoms about cobalt) are quite limited, as only the 1- or

3-hydroxyl oxygens are conveniently placed for chelation reactions *via* chloride displacement. Such chelation would not place C^1 in a position suitable for glycosylamine formation onto co-ordinated ethane-1,2-diamine, although presumably it would not necessarily inhibit the Amadori reaction and so might ultimately give rise to the *cis*-$[Co(en)_2(NH_3)Cl]^{2+}$ complex[39] observed to be present in trace amounts in the reaction mixture (Fig. 3).

Fig. 4 shows a reaction scheme in which we rationalise the conversion of chelated *N*-(2-aminoethyl) glycosylamines of D-glucosamine to the various fructosamine and mannosamine derivatives we have characterised. The facts that the '$Co(en)_2$' moieties in these compounds have both Δ and Λ configurations for fructosamine but only Λ for mannosamine and that no Λ form of a glucosamine species has been detected suggest that a Λ form complex of glucosamine must be highly reactive and undergo irreversible conversion to the observed Λ form mannosamine and fructosamine complexes. In this regard, it is noteworthy that the fructosamine complex **7**, of Δ configuration, is generated in neutral solution from the glucosamine complex **3** without change of configuration about cobalt. Also possibly significant are the facts that the D-glucosamine-containing species **1** and **2** show facial binding of the three *N*-donor atoms of the glycosylamine whereas in all other species isolated, including the moderately reactive D-glucosamine derivative **3**,

Table 2 Torsion angles/° of the sugar residues. Atoms are denoted by number only, *O* italicised; all values are for the *absolute* chirality

Complex(es)	Atoms	Angle
1, 3	1–2–3–4	−62(4), −161.0(5)
	2–3–4–5	167(3), 177.4(5)
	3–4–5–6	176(3), 177.2(5)
2	*5*–1–2–3	66.5(5)
	1–2–3–4	−56.9(5)
	2–3–4–5	51.3(6)
	3–4–5–*5*	−50.6(7)
	4–5–*5*–1	56.8(5)
	5–*5*–1–2	−66.5(5)
4	*4*–1–2–3	−32.7(8)
	1–2–3–4	39.4(8)
	2–3–4–*4*	−33.9(8)
	3–4–*4*–1	14.2(3)
	4–*4*–1–2	11.9(8)
5, 8	*6*–2–3–4	−56.6(5), −49.3(4)
	2–3–4–5	52.5(5), 50.5(4)
	3–4–5–6	−53.7(5), −54.3(4)
	4–5–6–*6*	57.7(5), 57.6(4)
	5–6–*6*–2	−60.6(5), −56.7(4)
	6–*6*–2–3	59.8(5), 51.4(4)
6, 7	*n*–2–3–4	−32.8(12), −25.8(6)
	2–3–4–5	38.5(11), 37.6(5)
	3–4–5–*n*	−32.6(11), −37.7(6)
	4–5–*n*–2	13.4(12), 23.2(6)
	5–*n*–2–3	11.8(13), 1.4(6)

Table 4 Non-hydrogen positional parameters for complex **1**

Atom	*x*	*y*	*z*
Co	0.4414(3)	0.4532(4)	0.8373(5)
N(11)	0.518(2)	0.447(3)	0.988(3)
C(11)	0.487(3)	0.374(5)	1.112(6)
C(12)	0.411(2)	0.392(4)	1.125(5)
N(12)	0.369(2)	0.403(2)	0.986(3)
N(21)	0.365(1)	0.460(2)	0.684(3)
C(21)	0.408(2)	0.456(3)	0.538(4)
C(22)	0.476(2)	0.518(3)	0.539(4)
N(22)	0.515(2)	0.496(2)	0.688(3)
C(1)	0.319(2)	0.558(2)	0.704(4)
O(1)	0.260(1)	0.533(2)	0.807(3)
C(2)	0.365(2)	0.651(3)	0.759(4)
N(2)	0.414(1)	0.604(2)	0.875(3)
C(3)	0.318(2)	0.750(3)	0.815(4)
O(3)	0.365(1)	0.826(2)	0.879(2)
C(4)	0.272(2)	0.799(3)	0.694(4)
O(4)	0.317(1)	0.856(2)	0.589(3)
C(5)	0.216(2)	0.875(3)	0.751(5)
O(5)	0.163(1)	0.819(2)	0.846(3)
C(6)	0.174(3)	0.930(4)	0.624(5)
O(6)*	0.115(4)	0.991(5)	0.688(7)
O(6')*	0.141(3)	0.863(5)	0.515(6)
Cl	0.4628(6)	0.2753(9)	0.785(1)
S(1)	0.1890(5)	0.2811(8)	0.748(1)
O(11)	0.148(2)	0.196(3)	0.674(4)
O(12)	0.184(1)	0.382(2)	0.669(3)
O(13)	0.262(2)	0.257(3)	0.769(4)
O(14)	0.144(2)	0.295(4)	0.888(5)
O(01)	0.505(2)	0.674(3)	1.127(5)
O(02)	0.346(2)	0.087(2)	0.616(3)

* Site occupancy factor = 0.5.

Table 3 Carbon-13 chemical shifts for sugars and sugar complexes. All spectra for dilute DCl solvent, external MeOH reference

Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}
α-D-Glucosamine[a]	89.4	54.6	69.9	69.9	71.9	60.7				
β-D-Glucosamine[a]	93.0	57.1	72.3	70.0	76.4	60.8				
α-D-Mannosamine[b]	91.1	55.3	67.7	67.1	72.8	61.2				
β-D-Mannosamine[b]	91.8	56.4	70.3	67.0	76.9	61.2				
α-D-Fructosamine f[c]	44.7	102.1	82.5	76.3	82.6	61.0				
β-D-Fructosamine f[c]	43.7	99.1	77.8	74.5	81.1	62.2				
α-D-Fructosamine p[c]	40.9	96.3	70.6	71.9	66.0	62.9				
β-D-Fructosamine p[c]	45.4	95.6	69.8	69.6	69.2	64.1				
1[d]	89.8	62.2	71.0	70.8	68.4	63.1	50.7	45.0	44.9	43.5
2[d]	89.2	57.5	79.4	74.9	69.5	60.9	45.5	45.1	45.0	44.8
3[d]	87.6	68.5	73.8	71.9	71.5	62.1	50.4	47.1	45.8	43.9
4[d]	87.0	66.2	81.4	75.0	67.8	63.1	47.0	46.9	43.8	43.4
5[d]	53.3	90.3	76.5	69.0	68.2	69.7	50.5	46.8	46.0	44.0
6[d]	53.6	98.1	86.9	84.1	73.6	60.8	52.5	46.5	44.3	44.0
8[d,e]	56.3	93.0	74.1	70.3	67.9	66.2	53.7	47.1	44.9	43.5

[a] D-Glucosamine = 2-amino-2-deoxy-D-glucopyranose (used as the hydrochloride salt). Assignments are based on the literature,[33] allowing for a uniform displacement of all our observed shifts by ≈0.5 ppm to higher fields relative to the mean literature figures. DEPT editing distinguished the C^6 resonance from those for C^1–C^5. [b] D-Mannosamine = 2-amino-2-deoxy-D-mannopyranose (as the hydrochloride salt). Chemical shift values are taken from the literature.[33] [c] Fructosamine = 1-amino-1-deoxy-D-fructose; f denotes the furanose form, p the pyranose. Chemical shift values are taken from the literature[34] for the acetate salt in D_2O. [d] Assignments are partly based on DEPT editing and comparisons with the free sugar spectra but for C^3–C^5, in particular, they are uncertain and the δ values have been given simply in order of decreasing chemical shift. Carbon atoms C^7–C^{10} are those of the ethanediamine residues but their particular identities are unknown. [e] COSY measurements allowed distinction of C^1 from ethane-1,2-diamine methylene carbons.

Table 5 Non-hydrogen positional parameters for complex **2**

Atom	*x*	*y*	*z*
Co	0.234 33(3)	0.764 74(4)	0.129 6(1)
N(11)	0.160 9(2)	0.780 4(3)	0.314 5(7)
C(11)	0.105 1(3)	0.708 1(5)	0.274(1)
C(12)	0.133 5(3)	0.618 0(5)	0.204(1)
N(12)	0.191 4(2)	0.634 7(3)	0.078 1(7)
N(22)	0.272 7(2)	0.897 4(3)	0.189 7(6)
C(22)	0.327 0(3)	0.891 1(4)	0.329 4(9)
C(21)	0.321 7(3)	0.797 0(4)	0.437 3(8)
N(21)	0.298 0(2)	0.713 0(3)	0.316 6(6)
C(1)	0.352 8(2)	0.657 2(3)	0.215 4(7)
C(2)	0.371 1(2)	0.710 2(3)	0.038 1(7)
N(2)	0.306 7(2)	0.740 2(3)	−0.055 6(5)
C(3)	0.417 1(3)	0.638 4(4)	−0.071 8(8)
O(3)	0.436 4(2)	0.686 3(3)	−0.239 9(6)
C(4)	0.478 9(3)	0.611 7(5)	0.049 6(9)
O(4)	0.515 6(3)	0.532 6(6)	−0.038 8(7)
C(5)	0.457 8(3)	0.575 6(4)	0.241 5(8)
O(5)	0.410 5(2)	0.643 7(3)	0.327 0(5)
C(6)	0.518 5(3)	0.568 8(5)	0.365 7(9)
O(6)	0.496 1(2)	0.531 6(4)	0.542 0(7)
Cl(1)	0.169 26(7)	0.835 98(9)	−0.093 7(2)
Cl(2)	0.268 12(8)	0.413 33(9)	0.142 9(2)
Cl(3)	0.357 74(6)	0.968 55(9)	−0.175 8(2)
O(01)*	0.479(2)	0.869(3)	0.457(5)

* Site occupancy factor = 0.46(4).

Table 6 Non-hydrogen positional parameters for complex **3**

Atom	*x*	*y*	*z*
Co	0.685 66(7)	0.5(−)*	0.810 60(5)
N(11)	0.676 6(5)	0.474 6(7)	0.942 2(3)
C(11)	0.817 5(7)	0.453(1)	0.988 3(4)
C(12)	0.905 6(7)	0.578(1)	0.946 2(5)
N(12)	0.877 8(5)	0.558 7(7)	0.844 2(4)
N(21)	0.493 9(5)	0.442 6(6)	0.778 5(3)
C(21)	0.427 2(6)	0.586 4(8)	0.725 2(4)
C(22)	0.473 9(7)	0.743 5(8)	0.776 8(5)
N(22)	0.623 2(6)	0.733 5(7)	0.805 2(4)
C(1)	0.486 0(6)	0.273 5(7)	0.731 5(4)
O(1)	0.461 2(4)	0.152 4(5)	0.795 8(3)
C(2)	0.627 3(6)	0.237 5(7)	0.702 8(4)
N(2)	0.723 4(5)	0.264 7(6)	0.788 8(3)
C(3)	0.669 3(6)	0.356 0(7)	0.629 1(4)
O(3)	0.711 6(4)	0.509 0(7)	0.680 1(2)
C(4)	0.784 6(6)	0.292 8(8)	0.576 8(4)
O(4)	0.900 5(5)	0.263 1(7)	0.642 4(3)
C(5)	0.818 4(6)	0.411 4(8)	0.501 2(4)
O(5)	0.705 7(5)	0.429 3(8)	0.431 8(3)
C(6)	0.936 8(8)	0.353(1)	0.452 7(5)
O(6)	0.960 7(5)	0.463 0(7)	0.378 5(3)
N(01)	0.339 5(5)	0.493 7(9)	1.004 2(3)
O(11)	0.388 1(6)	0.355 4(7)	0.984 2(5)
O(12)	0.379 2(7)	0.621 3(8)	0.967 7(5)
O(13)	0.254 0(4)	0.502 1(9)	1.060 7(3)
N(02)	1.126 9(6)	0.236 9(8)	0.812 8(4)
O(21)	1.171 0(6)	0.378 0(9)	0.802 0(5)
O(22)	1.189 7(5)	0.110 8(8)	0.787 4(4)
O(23)	1.018 2(4)	0.215 3(7)	0.848 6(3)
N(3)	0.653 2(7)	0.817 9(8)	0.540 8(5)
O(31)	0.712 7(8)	0.827(1)	0.613 4(5)
O(32)	0.582 7(7)	0.690 9(8)	0.513 1(5)
O(33)	0.670(1)	0.924(1)	0.479 1(6)
O(01)	0.898 6(6)	0.895 4(7)	0.778 1(4)

* Defines origin.

the three *N*-donor atoms of the quadridentate glycosylamine ligands are meridional. A rationalisation of these is that formation of an imine double bond at C^1 of D-glucosamine, a plausible first step in the rearrangements observed, could well

Table 7 Non-hydrogen positional parameters for complex **4**

Atom	*x*	*y*	*z*
Co	0.432 2(1)	0.875 9(1)	0.437 84(1)
N(11)	0.379 2(8)	1.079 8(8)	0.444 72(9)
C(11)	0.244(1)	1.123(1)	0.431 3(1)
C(12)	0.269(1)	1.065(1)	0.408 6(1)
N(12)	0.319 2(7)	0.905 8(8)	0.410 57(9)
N(21)	0.546 7(8)	0.845 6(8)	0.464 66(9)
C(21)	0.708(1)	0.841(1)	0.458 6(1)
C(22)	0.733(1)	0.956(1)	0.440 9(1)
N(22)	0.621 0(7)	0.926 6(7)	0.423 65(9)
C(1)	0.483(1)	0.708(1)	0.476 9(1)
C(2)	0.341(1)	0.664(1)	0.464 9(1)
N(2)	0.267 8(8)	0.794 1(8)	0.454 9(1)
C(3)	0.404 4(9)	0.564 6(9)	0.446 9(1)
O(3)	0.471 2(6)	0.666 9(6)	0.431 45(7)
C(4)	0.526(1)	0.481(1)	0.459 3(1)
O(4)	0.582 9(7)	0.588 1(6)	0.475 45(8)
C(5)	0.656(1)	0.420 7(9)	0.445 9(1)
O(5)	0.592 1(7)	0.307 2(6)	0.431 95(9)
C(6)	0.778(1)	0.361(1)	0.459 9(1)
O(6)	0.723 0(7)	0.259 3(7)	0.475 66(9)
S(1)	1.019 4(3)	0.433 4(3)	0.397 02(3)
O(11)	0.954 8(8)	0.436 5(8)	0.375 31(9)
O(12)	0.949 3(8)	0.329 1(7)	0.411 45(9)
O(13)	1.179 9(7)	0.423 5(8)	0.396 8(1)
S(2)	0.968 3(3)	0.649 2(3)	0.409 52(4)
O(21)	1.045 1(8)	0.747 6(8)	0.394 6(1)
O(22)	0.807 2(7)	0.663 3(7)	0.407 4(1)
O(23)	1.024 5(9)	0.649 8(9)	0.431 8(1)
S(3)	0.060 5(3)	*x* + 1	$\frac{1}{2}$
O(31)*	0.058(2)	0.957(2)	0.519 4(3)
O(32)*	−0.045(1)	1.186(1)	0.506 7(2)
O(33)*	0.038(2)	1.009(2)	0.479 3(3)
S(4)*	0.274 0(5)	1.161 3(5)	0.501 56(7)
O(41)*	0.256(3)	1.280(4)	0.485 0(4)
O(42)*	0.376(2)	1.043(1)	0.493 3(2)
O(43)*	0.303(4)	1.212(4)	0.523 9(4)
O(01)	0.429 5(8)	0.586 8(8)	0.393 09(8)
O(02)*	0.636(2)	0.373(2)	0.385 0(2)
O(03)*	0.693(2)	0.207(3)	0.395 8(2)
O(04)*	0.844(2)	1.047(2)	0.386 3(2)
O(05)*	0.088(1)	0.519(1)	0.505 7(2)

* Site occupancy factor = 0.5.

be more facile at a 'planar' central nitrogen of a *mer* donor atom array than a 'bent' nitrogen of a *fac* array,[30,38] so that *mer* D-glucosamine derivatives would disappear more rapidly from the initial product mixture. Indeed, the simplest interpretation of the observed product configurations would be that meridional binding of the glycosylamine N_3 unit is a prerequisite to rearrangement. Further, in the presumed enediamine intermediate (Figs. 3 and 4) through which the crucial steps of the rearrangement may occur, C(2) must also become trigonal planar, causing the attached polyhydroxy chain of the sugar to project out from the metal-ion centre and making chelation through hydroxyl groups essentially impossible except through a very large ring. The converse of this is that chelation through a hydroxy group may inhibit rearrangement by favouring a pyramidal form at C(2), and this may explain the apparently high reactivity of the Λ form of the glucosamine complex, since the configuration at C(2) is such that even in the complex where the *N*-(2-aminoethyl) glycosylamine is bound tridentate the hydroxyalkyl chain is in an orientation where chelation is unfavourable. Thus, in this complex in particular an especially facile conversion to the enediamine and hence to other sugars might be expected. Chelation that becomes possible after inversion at C(2) (to give mannosamine) may explain some 'trapping' of the Λ products in the form of a mannosamine derivative as well as a fructosamine

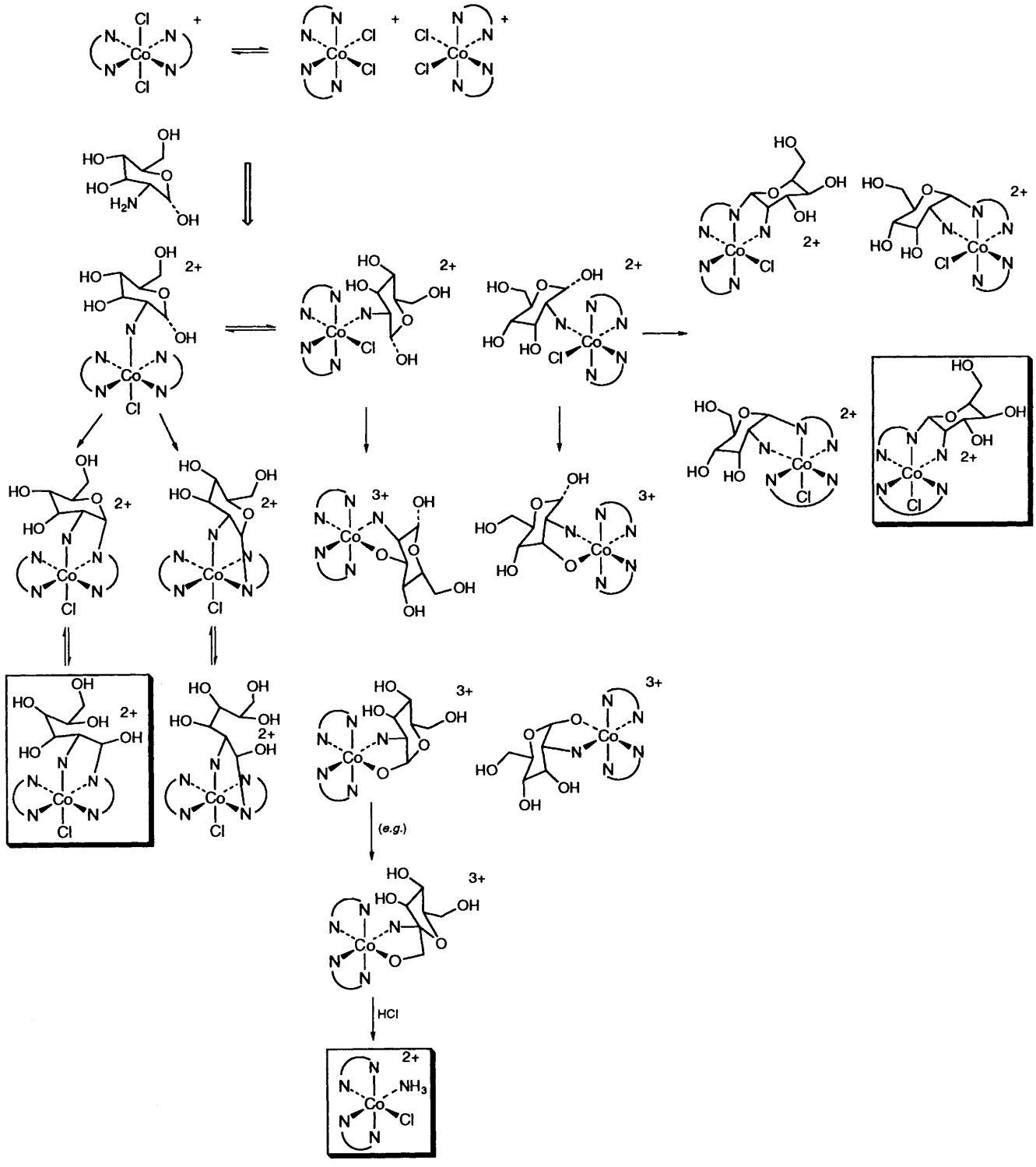

Fig. 3 Possible reaction pathways to the minor products observed in the present reactions. Structurally characterised species are shown boxed. For clarity, ethane-1,2-diamine chelate rings are shown as hoops and hydrogens are omitted from donor atoms

derivative (where again chelation is possible, as, of course, is shown by the crystal structure). All the Δ form products isolated, including the glucosamine derivative **3**, show hydroxyl group chelation, and, significantly, no Δ-form mannosamine complex, where again chelation would be difficult (Fig. 4), is detected.

Despite the fact that our isolation of the compounds described above may well reflect their relative lack of reactivity, it is possible to observe some transformations in basic solution. Thus, complexes **1**, **5**, **6** (=**7**) and **8** were recovered unchanged after reaction in 0.1 mol l^{-1} Na_2CO_3 for 10 min followed by acidification and evaporation to dryness, while the same treatment of **2** resulted in the formation of three new compounds (as established by ^{13}C NMR spectroscopy of the residue, assuming any particular complex would give rise to 10 signals), of **3** gave two new compounds, possibly imine or enediamine species, as well as recovered **3**, and of **4** gave mainly unchanged complex but also a minor amount of a

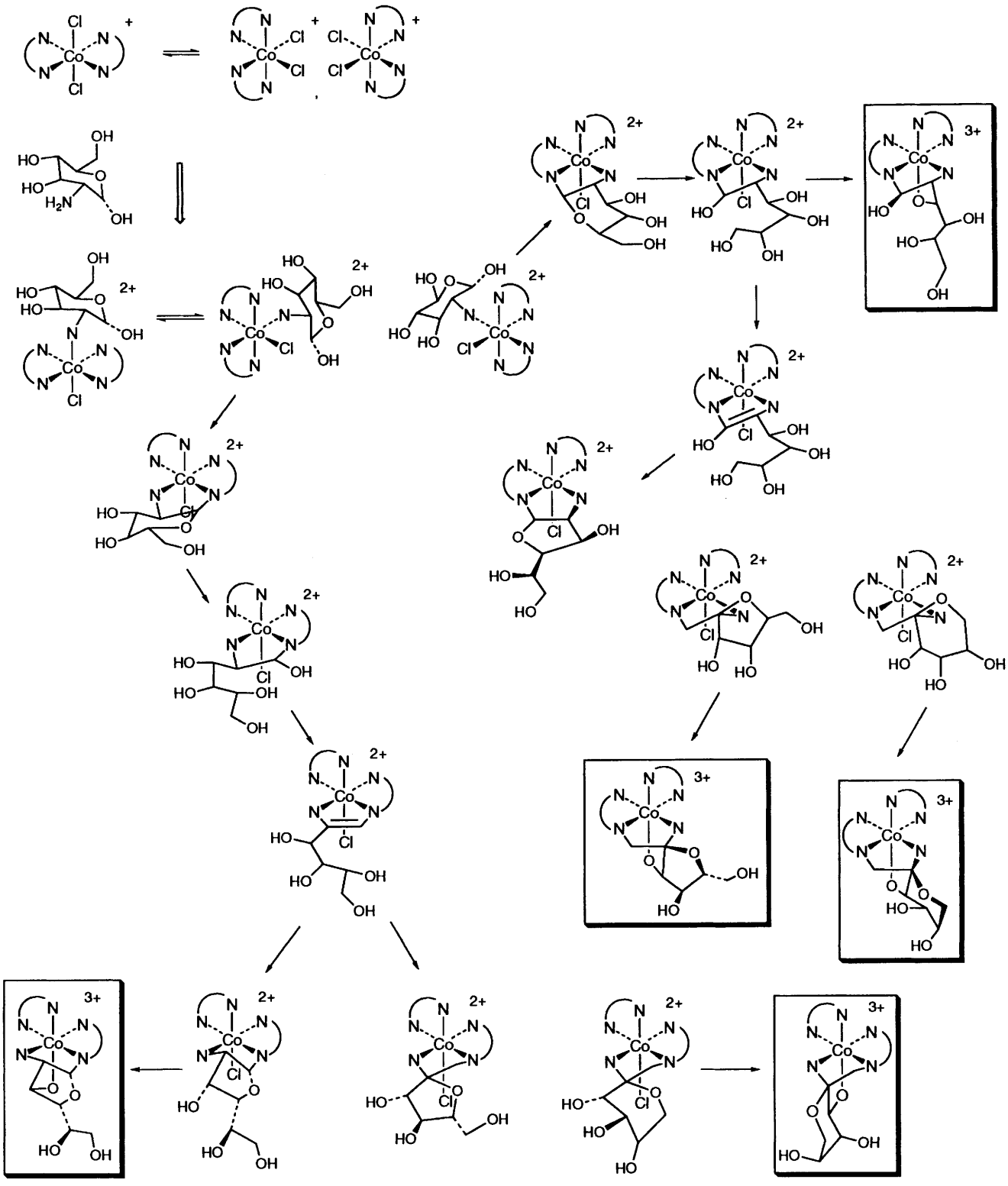

Fig. 4 Possible reaction pathways to the major products observed in the present reactions. Structures for all the sugar complexes are shown in the same orientations as used for crystal structures (Fig. 1). Again, boxes indicate the species crystallographically characterised and the formulae are simplified to allow focus on the sugar characteristics

new species. As noted above, we are currently conducting an extensive thermodynamic and kinetic investigation of all these processes, with the ultimate aim of establishing applications in synthesis.

Acknowledgements

We gratefully acknowledge support of this work by the Australian Research Council. We thank Dr. Lindsay Byrne for considerable assistance in the recording of NMR spectra.

Table 8 Non-hydrogen positional parameters for complex **5**

Atom	*x*	*y*	*z*
Co	0.313 58(6)	0.500 00	0.239 42(5)
N(11)	0.403 5(4)	0.346 0(4)	0.328 7(4)
C(11)	0.530 1(7)	0.324 2(9)	0.271 0(7)
C(12)	0.553 0(7)	0.391 5(8)	0.160 6(8)
N(12)	0.466 2(4)	0.501 2(5)	0.128 9(3)
N(21)	0.159 7(3)	0.503 2(5)	0.346 5(3)
C(21)	0.041 9(5)	0.458 4(5)	0.262 1(5)
C(22)	0.089 3(6)	0.342 3(5)	0.185 9(6)
N(22)	0.210 2(4)	0.384 3(4)	0.120 0(4)
C(1)	0.150 1(5)	0.638 6(5)	0.403 6(4)
C(2)	0.269 6(4)	0.719 3(4)	0.365 7(4)
N(2)	0.382 9(4)	0.627 8(4)	0.372 2(3)
C(3)	0.261 1(4)	0.765 1(4)	0.222 3(4)
O(3)	0.235 5(3)	0.648 9(3)	0.148 0(3)
C(4)	0.157 0(5)	0.872 6(4)	0.200 9(4)
O(4)	0.157 6(3)	0.922 8(3)	0.071 1(3)
C(5)	0.185 5(5)	0.984 4(5)	0.303 7(5)
O(5)	0.301 4(3)	1.059 7(3)	0.279 1(3)
C(6)	0.195 1(5)	0.926 3(5)	0.440 9(5)
O(6)	0.297 0(3)	0.826 3(3)	0.454 0(3)
S(1)	0.330 4(1)	0.452 8(1)	0.721 4(1)
O(11)	0.393 5(4)	0.429 9(5)	0.849 2(3)
O(12)	0.223 7(4)	0.548 9(4)	0.716 8(4)
O(13)	0.423 1(3)	0.474 0(4)	0.619 4(3)
S(2)	0.235 5(1)	0.269 9(1)	0.667 6(1)
O(21)	0.149 9(4)	0.239 7(4)	0.772 5(3)
O(22)	0.343 4(4)	0.177 3(4)	0.658 7(4)
O(23)	0.161 8(4)	0.295 4(4)	0.544 0(3)
O(01)	0.313 9(4)	0.149 3(4)	0.996 2(3)
O(02)	0.073 3(3)	0.582 5(4)	0.940 5(3)

Table 9 Non-hydrogen positional parameters for complex **6**

Atom	*x*	*y*	*z*
Co	0.577 32(7)	0.764 1(1)	0.967 4(2)
N(11)	0.511 2(4)	0.818(1)	0.834(1)
C(11)	0.457 5(6)	0.779(1)	0.921(2)
C(12)	0.463 8(6)	0.791(1)	1.110(2)
N(12)	0.523 3(4)	0.747(1)	1.162(1)
N(21)	0.630 7(4)	0.782 5(9)	0.766(1)
C(21)	0.674 7(6)	0.868(1)	0.823(2)
C(22)	0.642 6(7)	0.970(1)	0.906(2)
N(22)	0.600 9(4)	0.918 6(8)	1.036(2)
C(1)	0.652 2(5)	0.667(1)	0.705(2)
C(2)	0.635 7(5)	0.581(1)	0.850(2)
O(5)	0.646 7(4)	0.468 0(8)	0.801(1)
N(2)	0.573 0(4)	0.605 5(8)	0.888(1)
C(3)	0.668 0(5)	0.602(1)	1.024(2)
O(3)	0.638 2(3)	0.691 3(7)	1.116(1)
C(4)	0.665 1(5)	0.485(1)	1.111(2)
O(4)	0.710 2(4)	0.475 2(9)	1.236(1)
C(5)	0.673 6(5)	0.406(1)	0.948(2)
C(6)	0.646 6(7)	0.287(1)	0.963(2)
O(6)*	0.663 3(9)	0.227(2)	0.810(3)
O(6')*	0.581 9(7)	0.321(2)	0.987(2)
Cl(1)	0.453 3(5)	0.453 3(6)	0.031(1)
Br(1)*	0.453(1)	0.456(2)	0.041(4)
Cl(2)*	0.715 8(5)	0.839 7(6)	0.325(2)
Br(2)*	0.707(2)	0.851(5)	0.333(7)
Cl(3)	0.503 2(1)	0.600 4(3)	0.522 1(5)
O(01)	0.336 7(5)	0.591(1)	0.124(2)
O(02)	0.688 0(4)	0.306(1)	0.474(1)

* Site occupancy factors: O(6), O(6') 0.5, Cl(1) 0.800(9), Br(1) 1–0.800(9), Cl(2) 0.88(1), Br(2) 1–0.88(1).

Table 10 Non-hydrogen positional parameters for complex **7**

Atom	*x*	*y*	*z*
Co	0.058 07(9)	0.500 00	0.175 67(7)
N(11)	0.050 8(6)	0.642 8(5)	0.083 1(5)
C(11)	0.042 2(9)	0.622 7(6)	−0.062 0(7)
C(12)	−0.075 5(9)	0.524 2(6)	−0.095 2(7)
N(12)	−0.017 4(7)	0.437 9(5)	−0.001 3(6)
N(21)	0.134 7(6)	0.568 8(4)	0.346 9(5)
C(21)	−0.008 2(8)	0.550 8(6)	0.443 1(7)
C(22)	−0.178 3(9)	0.579 8(6)	0.346 7(7)
N(22)	−0.184 1(6)	0.518 4(5)	0.219 0(5)
C(1)	0.316 6(8)	0.531 3(5)	0.400 6(6)
C(2)	0.353 0(7)	0.435 2(5)	0.314 3(6)
N(2)	0.310 6(6)	0.473 2(4)	0.175 6(5)
C(3)	0.230 6(7)	0.337 7(5)	0.330 7(5)
O(3)	0.068 3(5)	0.355 1(3)	0.250 0(4)
C(4)	0.343 7(7)	0.239 2(5)	0.305 0(6)
O(4)	0.285 9(5)	0.143 3(4)	0.365 2(4)
C(5)	0.526 4(8)	0.280 1(5)	0.373 1(6)
O(5)	0.528 7(5)	0.396 4(4)	0.342 8(4)
C(6)	0.684 0(8)	0.228 2(5)	0.323 1(6)
O(6)	0.840 7(6)	0.268 0(5)	0.396 1(5)
S(1)	0.481 9(2)	0.279 9(1)	−0.091 9(2)
O(11)	0.634 5(7)	0.311 0(5)	−0.002 3(6)
O(12)	0.324 5(6)	0.263 7(5)	−0.029 1(5)
O(13)	0.515 6(8)	0.192 7(5)	−0.179 2(5)
S(2)	0.420 3(3)	0.422 9(2)	−0.210 5(2)
O(21)	0.560 8(7)	0.437 0(5)	−0.289 0(6)
O(22)	0.424(1)	0.507 7(7)	−0.109 3(7)
O(23)	0.257 2(9)	0.401 4(8)	−0.286 2(8)
O(01)	0.141 1(9)	0.803 9(5)	0.318 3(7)

Table 11 Non-hydrogen positional parameters for complex **8**

Atom	*x*	*y*	*z*
Co	0.428 98(3)	0.611 36(3)	0.496 70(4)
N(11)	0.508 0(2)	0.702 5(3)	0.580 5(3)
C(11)	0.451 1(3)	0.771 8(3)	0.651 9(3)
C(12)	0.379 6(3)	0.702 4(4)	0.702 9(4)
N(12)	0.338 2(2)	0.639 0(3)	0.612 5(3)
N(21)	0.520 0(2)	0.583 7(2)	0.383 0(3)
C(21)	0.546 8(3)	0.471 7(3)	0.390 9(4)
C(22)	0.555 5(3)	0.446 5(3)	0.512 7(4)
N(22)	0.472 0(2)	0.484 5(3)	0.569 7(3)
C(1)	0.485 0(3)	0.618 4(3)	0.273 5(3)
C(2)	0.388 9(3)	0.664 6(3)	0.289 0(3)
N(2)	0.393 1(2)	0.723 6(3)	0.395 2(3)
C(3)	0.319 2(3)	0.577 0(3)	0.304 7(3)
O(3)	0.338 1(2)	0.531 5(2)	0.411 6(2)
C(4)	0.220 8(2)	0.614 9(3)	0.298 9(3)
O(4)	0.159 8(2)	0.530 2(3)	0.294 0(3)
C(5)	0.209 3(3)	0.680 5(3)	0.193 6(3)
O(5)	0.211 3(2)	0.614 6(3)	0.098 6(2)
C(6)	0.278 9(3)	0.767 1(3)	0.190 4(4)
O(6)	0.370 7(2)	0.726 8(2)	0.196 2(2)
Cl(1)	0.224 20(6)	0.848 34(8)	0.504 6(1)
Cl(2)	0.583 31(8)	0.853 27(9)	0.371 87(9)
Cl(3)	0.452 56(8)	0.195 0(1)	0.523 0(1)
O(01)	0.128 1(2)	0.444 5(3)	0.499 4(4)
O(02)	0.328 7(3)	0.337 0(3)	0.365 3(3)
O(03)	0.575 3(3)	0.566 8(4)	0.756 4(3)
O(04)	0.775 0(4)	0.551 8(5)	0.262 9(5)
O(05)*	0.355 0(6)	1.010 4(8)	0.386 8(7)
O(06)*	0.288(2)	1.076(2)	0.439(2)

* Site occupancy factors: O(05) = 0.73(2), O(06) 1.0–0.73(2).

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