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Sucrose bis(1,10-phenanthroline)cobalt (III). Predicted distortion at the octahedral center

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Abstract

The two 1,10-phenanthroline ligands in the mixed Δ-cobalt(III) complex with sucrose are in different environments relative to the sucrose ligand as shown by differences in their ^{1}H NMR signals and predicted by structural optimization. There is considerable congestion between the glucose moiety and one of the phenanthrolines in the Δ-complex, and the interactions which stabilize it, relative to a Λ-complex, are analyzed. Differences in ^{1}H chemical shifts of the phenanthrolines are related to their mutual interactions and those with the glucose moiety of the sugar, which lead to π-shielding in some of its ^{1}H NMR signals. Absorption and circular dichroism (CD) spectra are analyzed with assignment of the electronic transitions.

Keywords: Carbohydrates; Cobalt complexes; Circular dichroism; Sucrose complexes; ^{1}H NMR; Semi-empirical calculations

1. Introduction

Sugars, and other polyols, complex with metal ions [1,2], and we have examined mixed complexes of sugars with cobalt(III)bis(1,10-phenanthroline), ($Co(phen)_2$) [3]. Ligating groups of the sugar residue in a complex are identified by the aliphatic ^{1}H NMR signals [3–5] without interference by phenanthroline signals in the aromatic region. Configuration at Co(III) is established from the circular dichroism (CD) spectrum [6] and with some sugars both Δ- and Λ complexes have been identified [7,8].

We have to date emphasized structures and configurations of the sugar residues in these complexes rather than interactions with phenanthroline, which is, however, a convenient ligand because the sign sequence of the CD signals identifies configuration at Co(III) [6], it is relatively rigid and approximately planar, and its ^{1}H NMR signals do not interfere with those of the sugar. For mixed complexes with galactose and arabinose [8] we used absorption and CD spectra to assign electronic transitions in the $Co(phen)_2$ residues [6,9]. Complexes of some reducing sugars with Co(III) are not very stable, and then examination of their NMR spectra is complicated by decomposition which generates free sugar whose signals overlap those of the complex, except of hydrogens near the ligating centers. Although we could not obtain uncontaminated samples of some mixed complexes, we could generally identify structures of the sugar residue and configuration at Co(III) by using both NMR and electronic spectroscopy. Decomposition also generates sugar-free phenanthroline complexes, which complicate analysis of ^{1}H NMR signals in the aromatic region, although these complexes are racemic and do not perturb the CD spectra. Therefore, we had no information on the equivalence, or otherwise of the phenanthrolines. However, the complex of sucrose with $Co(phen)_2$ can be isolated as a stable solid [10] with the Δ-configuration at Co(III) and ligation by O-2(g) and HO-1(f) of the sugar in a dicationic complex [10b]. The ^{1}H spectrum of this complex had the expected ratio of aliphatic to aromatic signals, no indication of decom-

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position, and examination of the ^{1}H NMR signals of this complex in the aromatic region should provide evidence on orientations of the two phenanthrolines with respect to the sugar. The conformation of crystalline sucrose [11] is such that complexation at an octahedral center does not markedly distort the sugar residue [10].

The ^{1}H NMR signals of the sucrose moiety showed that the face of one phenanthroline is sufficiently close to the glucose residue to allow observation of a nuclear overhauser effect (NOE) between H-2(g) and one phenanthroline hydrogen, and there was a second NOE involving OH-1(f) of the fructose residue and a hydrogen of the other phenanthroline ligand. Both aromatic hydrogens are at positions adjacent to nitrogens, and the phenanthrolines are in different environments relative to the sugar [10b], but there was no information on the other ^{1}H NMR signals. These conclusions were consistent with structural optimization of the Δ-complex with semi-empirical PM3(tm) parameters [12,13], which gives the structure shown in Fig. 1. This structure was obtained by a slightly different optimization procedure from that used earlier [10b], and it is described later. Structures from the two procedures are superimposable. We designate phenanthroline A as *trans*- to O-2(g), phenanthroline B as *trans*- to HO-1(f) [10b], and phenanthroline positions are numbered 1–10 with N-1(A) and N-1(B) in a trans-relationship. The linkage of the fructose residue to Co(III) through a hydroxymethyl group ensures that the fructose ring is not in close contact with a phenanthroline group, but the linkage through O-2(g) brings the glucose residue very close to phenanthroline B.

The ^{1}H NMR signals of the mixed sucrose complex in the aromatic region and other spectral evidence showed that this complex is sufficiently stable in solution to allow examination of all the ^{1}H signals of the two

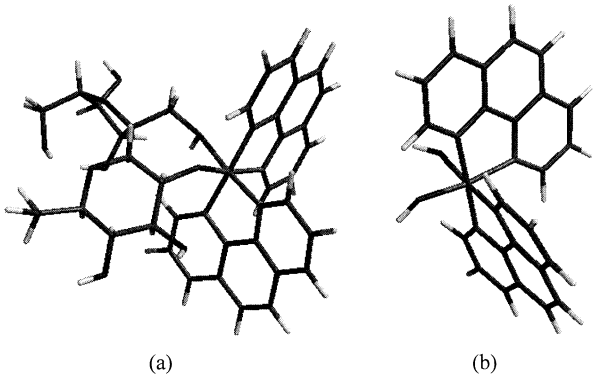

Fig. 1. Reoptimized geometry of the Δ-complex. Phenanthroline ring A is attached to the upper coordination site of Co(III) with the sucrose residue on the left and ligated glucose at the front, B is attached to the lower site of Co(III): (a) complex; (b) with sucrose ligand removed for clarity.

phenanthroline ligands and their interactions with the sugar residue, which had not been feasible with monosaccharide complexes [3,8,10]. Ito et al. had assigned the aromatic ^{1}H signals in a mixed complex of Co(phen)$_2$ with ethylenediamine, where the phenanthrolines are identical [14]. They showed that hydrogens in one part of a phenanthroline are close to the face of the other phenanthroline with consequent π-shielding and chemical shifts at position 9 are lower than at position 2 by approximately 2 ppm.

The ^{1}H signals of OH groups of the sugar residue had been examined in DMSO, where there was less overlap of the aromatic ^{1}H NMR signals than in D_2O, which simplifies assignment. Aliphatic ^{1}H signals were similar in the two solvents, and we assumed that the structure did not change, but we planned to confirm that assumption by comparing the CD spectra in H_2O and DMSO [10b]. We were also interested in comparison of the absorption and CD spectra of the sucrose complex and other mixed monosaccharide complexes, because positions of the CD extrema seemed to be insensitive to monosaccharide structure [3,8]. We have been unable as yet to obtain crystals of these mixed complexes suitable for X-ray crystallography and, therefore, rely on evidence from CD and NMR spectroscopy [6,8,10], and use semi-empirical treatments to predict overall structures consistent with spectral and other data.

2. Results and discussion

2.1. NMR spectroscopy

The ^{1}H NMR spectrum in the aromatic region in either D_2O or DMSO-d_6 shows signals of 16 hydrogens, with some overlap (Table 1). Signals of H-2 (A) and H-2(B), which had been assigned [10b], have the highest chemical shifts [14], and their $H_{2,3}$ coupling constants (Table 1) show that they are adjacent to phenanthroline nitrogens [15]. Following the Rules of Ito et al. [14] we conclude that signals with the lowest chemical shifts are of H-9 (A, B), consistent with their coupling constants [14,15], but these observations do not distinguish between signals of phenanthrolines A or B.

Hydrogens 3(A) and 4(A), and 3(B) and 4(B), are assigned from the COSY spectrum and decoupling in both DMSO-d_6 and D_2O. We applied a similar approach to hydrogens at positions 7, 8 and 9 in each phenanthroline, but to assign them to phenanthroline A or B we had to establish connectivities through positions 5 and 6 for each phenanthroline.

Signals in DMSO-d_6 are sufficiently separated that we could use NOE to establish connectivities within each phenanthroline. We irradiated one H-5, which could be in either ring, and saw an NOE in one, but not the other, H-4 signal, and then irradiated the other H-5 and saw

Table 1
^{1}H NMR spectra of the phenanthroline groups [a]

	Position							
	2	3	4	5	6	7	8	9
In DMSO-d_6								
δ, (ppm), A	9.86	8.51	9.18	8.45	8.34	8.82	7.72	7.62–7.65
B	10.18	8.31	9.13	8.42	8.27	8.87	7.62–7.65	7.48
T1, s, A	1.6	2.1	2.4	2.3	2.0	2.4	2.1	
B	1.1	2.1	2.3	2.2	1.7	2.3		2.2
Coupling	2.3	3.4	5.6	7.8	8.9			
J, (Hz), A	5.0	8.0	9.0	8.0	5.0			
B	5.5	8.5	9.0	8.0	5.0			
In D_2O								
δ, (ppm), A	9.78	8.43	9.10	8.31–8.36	8.19–8.24	8.68	7.59	7.48
B	10.01	8.31–8.36	9.08	8.31–8.36	8.19–8.24	8.66	7.55	7.38
Coupling	2.3	2.4	3.4	5.6	7.8	7.9	8.9	
J, (Hz), A	5.5	1.0	8.0	9.0	8.0	0.8	5.5	
B	5.5	1.0	7.0	9.0	8.0	0.8	5.5	

[a] At 500 MHz, referred to DMSO or TSP in D_2O.

the NOE in the other H-4 signal, thus assigning H-5 (A and B). Connectivities between H-5 and -6 (A and B) where then assigned by the COSY spectrum and decoupling. Connectivities between H-6 and -7 of rings A or B were similarly established by observing the appropriate NOE after irradiating H-7 of either ring A or B. This procedure gives assignments of all the ^{1}H phenanthroline signals and chemical shifts, coupling constants and T_1 values are in Table 1.

Assignments of the ^{1}H NMR signals in D_2O are based on the COSY spectrum, values of coupling constants [15], and decoupling at positions 2–4, 5–6, 7–9, the rules given by Ito et al. [14], and the assumption that sequences of chemical shifts will be the same in DMSO-d_6 and D_2O (Table 1). We saw long-range coupling for some phenanthroline signals in D_2O, but not in DMSO-d_6, probably because its higher viscosity broadens signals sufficiently to obscure weak coupling.

For a given phenanthroline ^{1}H chemical shifts vary qualitatively as predicted [14], and differences between values in rings A and B (Table 1) are governed by mutual interactions between the phenanthrolines and those with the glucose and fructose residues of the sugar. Differences in the ^{1}H NMR chemical shifts for a given phenanthroline, and between hydrogens at similar positions in the two rings, are largest for H-2 and -3 which are nearest to the sugar residues but are in different environments (Fig. 1 and Table 1).

2.2. Absorption and CD spectra

Spectra of the Δ-complex in the UV and visible regions are in Table 2. Positions of the CD extrema and shoulders are similar in H_2O and DMSO, although solvent absorbance by DMSO limits the low wavelength range. Positions and signs of the CD signals are similar to those of Δ-complexes of $Co(phen)_2$ with α-D-galactose and β-D-arabinose [8], where the sugar is bonded to Co(III) in a five-membered ring as compared with the eight-membered ring in the sucrose complex, i.e. they depend on the atoms bound to Co(III) rather than on the ring size. Following classical work on the electronic spectra of mixed complexes with $Co(phen)_2$ [9], as applied to the galactose and arabinose complexes [8], assignments in water are: λ, (nm), and ν, (cm^{-1}) in parentheses: phenanthroline transitions: 229, 241 (4.37×10^4, 4.15×10^4); β; 267, 281 (3.75×10^4, 3.56×10^4), p; 297 (3.37×10^4), α. Co(III), d–d transitions: 323, 363 (3.01×10^4, 2.75×10^4), ^1T_2g; 413, 513 (2.42×10^4, 1.95×10^4), ^1T_1g; approximately 610 (1.64×10^4), ^3T_2g. Assignments in DMSO are as in H_2O, within the wavelength range that can be examined, and there is a positive CD signal at < 260 nm (Table 2), although we cannot specify its location. In both solvents excitonic effects confirm that two phenanthrolines are bound to Co(III) and the sign sequence establishes the Δ-configuration [6,8]. The CD signals at 332 and 363 nm assigned to the ^1T_2g state represent forbidden transitions for a complex with strict octahedral symmetry, but in these mixed complexes there is distortion of the octahedral Co(III).

The CD signals in the UV are at similar wavelengths in H_2O and DMSO, confirming that there is no solvent effect on configuration, but those in the visible are red-shifted in DMSO, and apparently solvent effects upon energies associated with the d–d transitions are larger than those with the phenanthrolines. There is a shoulder at 413–436 nm in the absorption spectrum in DMSO, which was not seen in H_2O [10b].

Table 2
Absorption and CD spectra of Δ-[Co(III)(phen)$_2$(sucrose)]Cl$_2$

H_2O [a]				DMSO			
Absorption		CD		Absorption		CD	
λ (nm)	log ε	λ (nm)	$\Delta\varepsilon$	λ (nm)	log ε	λ (nm)	$\Delta\varepsilon$
227	5.03	229	−5.5				
		241	+8.6				
		267	+11.3	271	4.63	260	+10.9
270	4.67	281	−15.4			284	−14.2
		297sh	−5.7	298sh	4.32	297sh	−6.5
295sh	4.31	323	+3.3	329sh	3.78	346	+3.6
329sh	3.67	363	−1.8			389	−0.32
		413	+3.6			436	+4.3
519	2.15	513	−6.8	515	2.25	518	−6.7
		610sh	−0.27			620sh	−0.52

[a] From ref. [10b].

The quantitative treatment applied to electronic transitions of mixed complexes of Co(phen)$_2$ with α-galactose or β-arabinose [8] applies to spectra of the sucrose complex in terms of similar energy levels on the basis of similar wavelengths of extrema and shoulders in the CD spectra.

2.3. Geometrical optimization

The structure of the Δ-sucrose complex had been treated by using semi-empirical PM3(tm) parameters (PC Spartan Plus 2.0, Wavefunction) [13] which had been parameterized for transition metal ions, including Co(III), but only the geometry of the sucrose-Co(III) residue had been discussed [10b]. The predicted O-2(g)–Co–O-1(f) bond angle of 92.8° was higher than in a strictly octahedral complex. We, therefore, repeated the optimization with this angle constrained to 90°, which gave a less favorable heat of formation by approximately 10 kcal mol^{-1}, but removal of the constraint and re-optimization gave the structure (Fig. 1) which is indistinguishable from the original and has the original bond angle at Co(III) indicating that the optimized structure was not in a false minimum. The heat of formation, rounded off to the fourth significant figure, is −1684 kcal mol^{-1} as found earlier [10b].

Predicted bond lengths and angles at Co(III) are given in Table 3 and [10b] for the Δ- and the hypothetical Λ-complex, which was not detected and whose formation is predicted to be disfavored, relative to the Δ- complex, by approximately 9 kcal mol^{-1} [10b].

2.4. Factors that control structure of the complex

The ^{1}H NMR and CD spectra of Δ-Co(phen)$_2$(sucrose) identify the configuration at Co(III) and the ligating groups of the sugar. The NMR spectra show

Table 3
Predicted bond lengths and angles of the Δ-complex

Bond distances (Å)	
O^--2(g)–Co	1.89 (1.85)
HO-1(f)–Co	2.03 (2.03)
N-1(A)–Co	1.93 (1.93)
N-10(A)–Co	1.96 (1.96)
N-1(B)–Co	1.93 (1.93)
N–10(B)–Co	1.90 (1.90)
Bond angles (°)	
O^--2(g)–Co–HO-1(f)	92.8 (82.2)
HO-1(f)–Co–N-1(A)	84.4 (97.4)
N-1(A)–Co–N-10(A)	89.9 (90.0)
N-10(A)–Co–N-10(B)	91.9 (92.3)
N-10(B)–Co–N-1(B)	89.7 (90.5)
N-1(B)–Co–O^-2(g)	99.4 (80.9)

Values for a hypothetical Λ-complex are in parentheses.

that the phenanthrolines are in different environments [10b] and we need to rationalize these observations.

Predicted values of the torsional angles ϕ (O-5(g)–C-1(g)–O-1(g) –C-2(f)) of 114.5° and Ψ (C-1(g)–O-1(g)–C-2(f)–O-5(f)) of −51.2° are not very different from those of crystalline sucrose, 107.8° and −44.8°, respectively, indicating that ligation does not markedly perturb the conformation of sucrose [10b,11]. However, it forces the glucose moiety into close proximity with phenanthroline B, as shown by the strong upfield shift of O*H*-3(g) (by ca. 1.4 ppm) [10b]. There is not room for H_2O to hydrogen-bond to OH-3 (g), but there may be hydrogen bonding to the π-system [16]. We note that geometrical optimization orients OH-3 (g) away from the face of phenanthroline B (Fig. 1), which does not agree with the NMR evidence [10b]. It appears that the semi-empirical PM3(tm) treatment does not take into account O–H–π hydrogen bonding. In a Λ-complex the sucrose conformation would be perturbed relative to

that of the free sugar [11], with $\phi = 131.1$ and $\psi = -22.5°$, consistent with the relatively low stability of this hypothetical complex [10b].

The multiplicity of the ^{1}H NMR signal of H-3 (g) in the Δ-complex confirms that HO-3 (g) is oriented towards the face of phenanthroline B [10]b and the computed distance from O-3(g) to the phenanthroline face is approximately 2.7 Å. Accomodation of the glucose moiety with respect to phenanthroline B affects bond angles at Co(III) and optimization indicates that the N-1(A)–Co–N-1(B) axis is approximately linear, but not strictly orthogonal to the O^--2(g)–Co–HO-1(f) plane. This deviation from octahedral symmetry is consistent with the large predicted N-1(B)–Co–O^--2(g) angle, which reflects congestion between the glucose moiety and phenanthroline B, and the correspondingly smaller HO-1(f)–Co–N-1(A) angle (Table 2). In the optimized structure the fructose ring is not close to phenanthroline A because ligation is through the hydroxymethyl group, HO-1(f), whereas for the glucose residue it involves O^--2(g) [10b].

Deviations from strict octahedral symmetry place the phenanthrolines in different environments with respect to both the sugar residue and themselves, in accord with their different NMR signals (Table 1). These interactions may bow the phenanthroline rings. In a Co(III) bis-phenanthroline complex each phenanthroline rear face is close to H-9 of the other phenanthroline [14] consistent with variations in the ^{1}H chemical shifts (Table 1). In the Δ-sucrose complex H-9(B) is predicted to be approximately 2.7 Å from positions 1(A) and 2(A), and H-9(A) is a similar distance from positions 1(B) and 2(B). However, H-9(A) and H-9(B) are further from other positions of phenanthrolines B and A, respectively. These interactions between the phenanthrolines are, in general, opposed by those with the third bidentate ligand, e.g. sucrose, whose glucose moiety is very close to the front face of phenanthroline B [10b]. These opposing interactions can cause a phenanthroline to bow towards, or away from, sucrose and tilt in either direction. The magnitude of the bowing, or curvature, is indicated by the absolute sum of the torsional angles indicated by the heavy lines in Fig. 2(a). The tilt, with respect to the O–Co–O plane, is given by the absolute mean of the torsional angles indicated by the heavy lines in Fig. 2(b). The magnitude and direction of these distortions in a given phenanthroline depend on the balance between opposing effects of interactions with the sugar ligand and the second phenanthroline. Therefore, in the Δ-complex, where phenanthroline B is very close to the glucose moiety, predicted curvature is towards the sugar by 19°, and phenanthroline A, which is distant from the fructose ring, is curved away from the sugar by 15°, and is tilted modestly towards the sugar by approximately 6°, while ring B is tilted away by a similar extent. Thus phenanthroline A presents a convex, and B

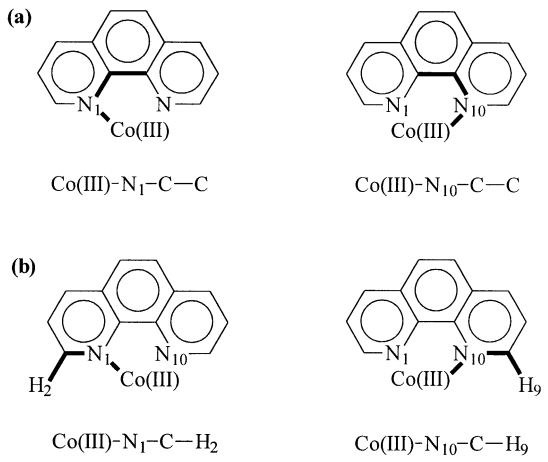

Fig. 2. Illustrations of estimated distortions of the phenanthroline group, c.f. Fig. 1. (a) Curvature of a group, the heavy lines indicate the noncoplanarities of Co(III)–N_1–C–C and Co(III)–N_{10}–C–C. (b) Tilt of a group, indicated by the torsional angles of Co(III)–N_1–C–H_2 and Co(III)–N_{10}–C–H_9.

a concave face towards sucrose, representing the balance between the interactions. Congestion between the glucose moiety and phenanthroline B more than offsets interactions from the rear with phenanthroline A. Predicted distortions for a hypothetical Λ-complex are similar in magnitude to those given above, except that curvatures are in the opposite sense.

These predicted deviations from planarity are responsible for differences between ^{1}H chemical shifts in the two phenanthroline rings (Table 1), even for hydrogens, which are distant from the sucrose moiety or the other phenanthroline (Fig. 1). These differences are more evident in DMSO-d_6 than in D_2O. The structure around Co(III) is very congested, as shown by examination of space-filling models, data not shown. Several distances between non-bonded atoms are within, or close to, the sum of the van der Waals radii.

So far as we are aware there is little information on structures of mixed bis-phenanthrolineCo(III) complexes from X-ray crystallography. There is distortion of octahedral symmetry in the carbonato complex [17] where the O–Co–O bond angle is low (ca. 69°), and Niederhoffer et al. report only modest bowing of the phenanthrolines, although Hennig et al. report deviations from planarity [18].

3. Experimental

Preparation and isolation of the mixed completes with Cl^- or I_3^- as counterion have been described, but the I_3^- salt was not used in the present work [10]. The ^{1}H NMR spectra were monitored on a Bruker DRX instrument, (300 MHz for ^{1}H) at 25 °C, or on a Varian Unity instrument (500 MHz for ^{1}H) at 21 or 25 °C for

the COSY spectrum and are referred to TSP (sodium 3-(trimethylsilyl)propanesulfonate) in D_2O ($\delta = 0$ ppm), or to DMSO ($\delta = 2.50$ ppm). Signals of the sucrose residue had been assigned [10]. There are uncertainties in chemical shifts of some of the phenanthroline signals in D_2O due to overlap (Table 1) but they do not affect the sequence of the chemical shifts.

The CD and absorption spectra in water are from [10], and those in DMSO were monitored at 25 °C on a Jobin–Yvon CD6 spectrometer, or, for the absorption spectrum, on a Unicam UV3 spectrometer, with freshly prepared solutions. With some monosaccharides the less stable diastereomer is formed initially and is gradually converted into the thermodynamically preferred complex [7,8], but only the Δ-complex was detected with sucrose.

4. Conclusions

The CD spectrum of $[Co(III)(phen)_2(sucrose)]Cl_2$ shows that it has the Δ-configuration in H_2O and DMSO and allows assignment of the electronic transitions. Differences in the ^1H NMR signals in the aromatic region show that the nonequivalent phenanthrolines differ in their non-bonding interactions with the sucrose moiety. The glucose residue is very close to one phenanthroline and structural optimization with the semi-empirical PM3 (tm) parameters indicates that there should be deviations from strict octahedral symmetry and planarity of the phenanthrolines consistent with differences in the ^1H NMR signals.

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