Sucrose bis(1,10-phenanthroline) cobalt(III). Comparison of semi-empirical and ab initio geometrical optimizations

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Abstract

The title compound (sucrose $Co(phen)_2$) is a dication with the Δ-configuration at Co(III) and ligation through O-2(g) and OH-1(f). Earlier geometrical optimization with semi-empirical PM3(tm) parameters had fitted most of the structural evidence from absorption, CD and NMR spectroscopy, although the site of deprotonation was predicted to be OH-1(f) rather than OH-2(g) as shown by NMR spectroscopy. Both HF and DFT treatments have now been used and they correctly predict deprotonation of OH-2(g), in agreement with experimental data. The HF 3-21(G*) and 6-31(G*) treatments incorrectly show OH-1(f) as planar, although it is pyramidal from ^{1}H NMR coupling constants, but a DFT LACVP*/BP/6-31(G*) optimization gives the correct geometry. The earlier PM3(tm) optimization indicated extensive bowing of both phenanthrolines due to steric repulsions, but the ab initio treatments indicate limited bowing which fits the NMR chemical shifts of the phenanthroline hydrogens.

Keywords: Sucrose complex; Cobalt (III) complex; Phenanthroline; Ab initio computation

1. Introduction

Sugars, other polyols and their amino derivatives form complexes with transition metal ions which can be identified in solution or isolated as crystalline solids [1,2]. We have examined mixed complexes with Co(III) bis(1,10-phenanthroline), $Co(phen)_2$, where structures of the sugar or other polyol moiety, and the configuration at Co(III), are established by NMR and circular dichroism (CD) spectroscopy. For some complexes both Δ- and Λ-complexes can be identified, but usually one diastereomer is dominant [3].

The conformation of crystalline sucrose [4] places OH-2(g) of the glucose moiety and OH-1(f) of the fructose moiety in close proximity which allows these oxygens to bond to Co(III) without markedly distorting either the sugar residue or the octahedral center [5a,5b]. The dianionic Δ-complex can be isolated as the water soluble chloride or the insoluble triiodide, and there is no evidence of a Λ-complex [5a]. Elemental analysis and electrolytic conductance showed that the complex is dicationic. The Δ-configuration at Co(III) was established from the circular dichroism spectrum in both water and DMSO [5a]. It was not possible to obtain material suitable for structural determination by X-ray crystallography, but ^{1}H NMR spectroscopy provided considerable structural evidence, for example, it confirmed that bonding to Co(III) involved O^--2(g) and OH-1(f) of the sugar. Comparison of the ^{1}H spin–spin coupling in sucrose and in the complex showed that neither the glucose nor the fructose rings are significantly perturbed by complexation [5a]. The conformation of sucrose, i.e., the geometrical relationship between the glucose and fructose residues is defined by the bond angle, C-1(g)–O–C-2(f), between the glucose

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and fructose residues, and the torsional angles, ϕ and ψ, O-5(g)–C-1(g)–O-1(g)–C-2(f) and C-1(g)–O-1(g)–C-2(f)–O-5(f), respectively (Fig. 1(a)), and our expectation was that these angles would not change markedly on formation of the complex, as was indicated by the earlier PM3(tm) optimization and is consistent with the higher level computations as shown later.

The geometry of the complex, initially optimized by using semi-empirical PM3(tm) parameters [5a], is similar to that shown in Fig. 1(b), which was obtained by a higher level DFT optimization. The optimized structure of sucrose is shown in Fig. 1(a) for comparison with that of the complex.

The initial PM3(tm) optimization had indicated that the Δ-complex should be strongly preferred over the Λ-complex, but it incorrectly predicted deprotonation of OH-1(f) rather than OH-2(g), as had been shown by ^{1}H NMR spectroscopy [5a]. An additional problem was that the predicted CH-3(g)–OH-3(g) torsional angle in the complex did not fit the evidence of a very low ^{1}H NMR coupling constant in DMSO. There was predicted distortion of both phenanthroline rings from planarity, which appeared to be due to competing interactions between a glucose or fructose residue with the front face of a phenanthroline, and a hydrogen of the other phenanthroline with the other (rear) face [5b]. In the structure shown in Fig. 1(b) the front face of the phenanthroline, designated A, is towards the hydroxyl group, OH-1(f), of the fructose residue and the rear face is towards H-9(B) of the second phenanthroline, designated B. The front face of phenanthroline B is towards the glucose residue, and the rear face is towards H-9(A) of phenanthroline A. The phenanthroline positions are numbered 1-10, and N1-(A) and N-1(B) are trans at Co(III). As in earlier work, phenanthroline A is shown in Fig. 1(b) as being attached to the upper coordination site of Co(III) with the sucrose residue on the left, and ligated glucose to the front, and B is attached to the lower site of Co(III) [5].

The PM3(tm) semi-empirical model has been parameterized to reproduce geometries of transition metal compounds, rather than energies [6–8], which may account for its inability to predict the correct position of deprotonation of sucrose in the dicationic complex. We have therefore carried out ab initio geometrical optimizations, using the following basis sets: HF 3-21(G*) and 6-31(G*), and DFT BP/6-31(G*), and at the higher levels we used LACVP* pseudopotentials at Co(III) [6,7].

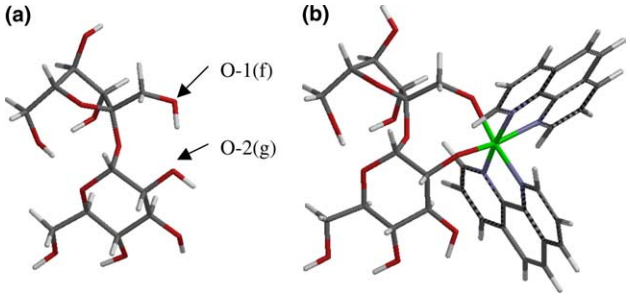

Fig. 1. Structures of sucrose (a) and the complex (b) from DFT optimizations. Phenanthroline ring A is attached to the upper coordination site of Co(III), and B is attached to the lower coordination site and is adjacent to the glucose residue.

2. Methods

Structures were optimized by using Spartan 04 (Wavefunction) starting from the geometrically optimized structures given earlier by using PM3(tm), and heats of formation were initially calculated by using the 3-21(G*) basis set, which provides adequate information under some conditions. Further information was obtained by using HF 6-31(G*) or DFT BP/6-31(G*) basis sets with LACVP* pseudopotentials [6,7]. Heats of formation are given to the nearest kcal mol^{-1}, as in the earlier work [5]. Assignments of all the ^{1}H NMR signals in D_2O and DMSO-d_6 had been made earlier [5], including those of the phenanthrolines, which were based on connectivities and the rules of Ito et al. [9].

3. Results and discussion

An initial comparison of conclusions from the semi-empirical, PM3(tm) and the HF treatments was based on the HF 3-21(G*) basis set which gave the Δ-complex energetically preferred over the Λ-complex by 18 kcal mol^{-1}; the corresponding difference from the PM3(tm) optimization had been 9 kcal mol^{-1} [5a]. There is no physical evidence for the existence of the Λ-complex of sucrose(phen)$_2$, either method of calculation fits this observation, and we did not examine the preference for the Δ-complex over the Λ-complex at higher levels. As noted, the PM3(tm) calculation had incorrectly indicated that deprotonation of OH-1(f) would be preferred over that of OH-2(g) by 3 kcal mol^{-1}, however, calculations at the HF 3-21(G*) and LACVP*/6-31(G*) levels indicate that deprotonation of OH-2(g) is preferred by ca. 5 kcal mol^{-1}, in agreement with experiment [5a]. The inability of the semi-empirical PM3(tm) treatment to predict relative energies for deprotonation is probably due to the reliance on geometrical criteria for parameterization for transition metals [6,7].

To this extent, calculation of energies for the HF optimized structures removes an anomaly in the PM3(tm) treatment [5a], but it introduces an error in the geometry of OH-1(f), which from the ^{1}H NMR spectral evidence in DMSO is pyramidal, in agreement with

the PM3(tm) optimized structure shown as Fig. 2 in [5a]. The ^{1}H signals at OH-1(f) and CH-2(f) had been assigned, and the coupling constants of OH-1(f) with H-1′(f) and H-1(f) in DMSO are 9.5 and 4.0 Hz, respectively, consistent with the predicted torsional angles of 170° and −75°, respectively, at the PM3(tm) level [5a]. The HF optimizations give a near planar OH-1(f), inconsistent with the NMR data [5a], and structures with torsional angles constrained to the values which fit the coupling constants are disfavored by 3 and 2 kcal mol^{-1} in 3-21 (G*) and 6-31 (G*) calculations, respectively. These constrained HF structures relax to the incorrect planar structure on removal of the constraint. Limitations of HF treatments of some pyramidal structures have been noted [6]. The structure re-optimized with the BP/6-31 (G*) basis set and LACVP* pseudopotentials for Co(III) had torsional angles of 176° and −68° between OH-1(f) and H-1′(f) and H-1(f), respectively, in reasonable agreement with the NMR coupling constants in DMSO and the earlier semi-empirical optimization [5a]. This structure from the DFT optimization with the estimated torsional angles is shown in Figs. 1(b) and 2 with H-1′(f) towards and H-1(f) away from the viewer and illustrates the pyramidal geometry at OH-1(f). Except as noted, the HF and DFT structures of the complex are in other respects similar, although only geometries from the latter and PM3(tm) are in Table 1 or the figures.

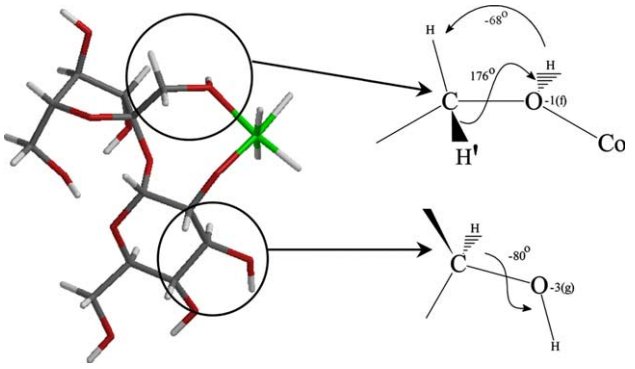

Fig. 2. Structure of the complex with the phenanthroline groups removed for clarity. The insets show the DFT computed torsional angles at CH–OH-1(f) and CH–OH-3(g).

Predicted geometries at Co(III) from the DFT optimization are shown in Table 1, and include comparison with values obtained earlier from the PM3(tm) treatment [5].

As for the parent sugar, the conformation of the sucrose moiety in the complex is defined by the bond angle, C-1(g)–O–C-2(f), between the glucose and fructose residues, and the torsional angles, ϕ and ψ [4], which are shown in Table 1 for the complex. We used DFT to optimize the geometry of sucrose to be consistent with the treatment of the geometry of the Co(III) complex. The structure at the BP/6-31(G*) level shown in Fig. 1(a) is similar to those in the crystal and from other treatments [4,10]. Computed values of the torsional angles ϕ and ψ are 108.6° (107.8°) and −35.6° (−44.8°), respectively, and the C-1(g)–O–C-2(f) bond angle is 117.8° (114.3°), and these are similar to values in the crystal [4], which are in parentheses. These values are similar to those calculated earlier [5,10] and are consistent with the original assumption that complexation does not significantly perturb the sucrose moiety. We note that our computation is for an isolated molecule and does not cover crystal packing or interactions with the environment [10]. However, ^{1}H NMR spectroscopy had shown that the conformation did not change significantly in going from D_2O to DMSO-d_6 [5a].

3.1. Semi-empirical and ab initio geometries

Computed geometries of the Δ-sucrose complex illustrated in Figs. 1 and 2, and Table 1, and given earlier [5],

Table 1
Geometry of Δ-sucrose $Co(phen)_2^{2+}$ [a]

Bonding to sucrose moiety			
Bond/torsional angle (°)			
O-2(g)–Co–O-1(f)	C-1(g)–O–C-2(f)	ϕ	ψ
95.1 (92.8)	117.7 (117.8)	112.0 (114.5)	−36.5 (−51.2)
Bond length/distance (Å)			
Co–O-2(g)	Co–O-1(f)	O-2(g)–O-1(f)	
1.88 (1.89)	2.03 (2.03)	2.89 (2.84)	
Bonding to phenanthroline nitrogens			
Bond angle (°)			
N-10(A)–Co–N-1(A)	N-10(B)–Co–N-1(B)		
81.6 (89.9)	84.6 (89.7)		
Bond length (Å)			
Co–N-1(A)	Co–N-10(A)	Co–N-1(B)	Co–N-10(B)
1.97 (1.93)	2.03 (1.96)	1.97 (1.93)	1.92 (1.92)

[a] Values in parentheses are from the PM3(tm) optimization [5a,5b].

show that PM3(tm) and DFT methods generate similar results, so far as the positions of bonding between sucrose and Co(III)$(phen)_2$ are concerned. However, the PM3(tm) incorrectly predicts the site of protonation in forming the dicationic complex, and indicates that there should be considerable bowing of both phenanthroline groups.

Each phenanthroline is sandwiched between H-9 of the other phenanthroline and either the glucose or fructose moiety. In terms of either semi-empirical (PM3(tm)), or ab initio optimizations using HF or DFT treatments H-9 of one phenanthroline is ca. 2.7 Å from the rear of the other phenanthroline, cf. [9]. The fructose ring is not very close to phenanthroline A, but the glucose ring is close to phenanthroline B, and O-3(g) is ca. 3.1 Å from the center of this ring, from the DFT optimization. Some of these predicted interatomic distances are therefore within the sum of the van der Waals radii and the half-thickness of an arene [11].

Bowing of a phenanthroline depends on the forms of the non-bonding interactions with either the sugar residue or the other phenanthroline, being repulsive or attractive. There is extensive evidence for non-classical –HO hydrogen bonding [12], and Nishio et al. [13] concluded that π-H–C interactions may be modestly attractive. The PM3(tm) optimization had indicated extensive bowing of both phenanthrolines, with phenanthroline A presenting a convex face and a modest tilt towards the sugar residue, and B presenting a concave face towards the sugar and a tilt away from it [5b]. The extent of bowing was given by the dihedrals between the outer rings of the phenanthrolines and the tilt was with respect to the N–Co–N plane, as illustrated in Fig. 2(a) and (b) in [5b] and discussed in detail in that reference. It appeared from this earlier optimization that repulsion from the rear between H-9(B) and phenanthroline A is greater than repulsion of the latter from the front by the fructose residue, but that for phenanthroline B repulsion by the glucose residue is dominant.

Predicted distortions of the phenanthrolines in the DFT optimization are significantly less than from the earlier PM3(tm) optimization [5b]. This is also the situation for the HF optimizations, although these geometries are not shown, because in this respect they are very similar to those in Figs. 1 and 3. The predicted bowing of phenanthroline A is almost zero rather than 15°, and the tilt is <1° rather than 6°, as given earlier, and the new DFT results are illustrated in Fig. 3, where (a) shows phenanthroline ring A viewed in profile with H1 and H2 projecting forward from the plane of the paper. Fig. 3(b) shows phenanthroline ring B viewed in profile with H5 and H6 projecting forward of the plane of the paper. The predicted bowing of phenanthroline B, as given by the sum of the dihedrals, is 16° rather than 19° and the tilt is 3° rather than 6°, estimated as outlined in [5b].

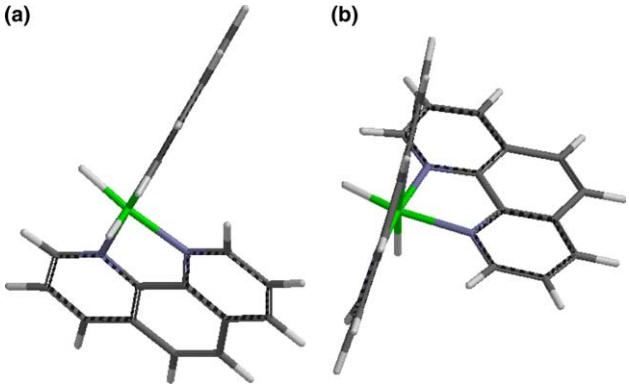

Fig. 3. Bowing of phenanthroline rings, shown in profile, with the sugar residue removed for clarity, and illustrating the predicted near planarity of ring A (a) and bowing of ring B (b).

It appears that in the PM3(tm) optimization the π-HO and π-H–C interactions are treated as repulsive, with consequent distortion of both phenanthrolines, whereas repulsion is less evident in the ab initio optimizations. There is limited direct physical evidence regarding geometries of phenanthroline groups in mixed Co(III) complexes and possible distortions due to interactions with adjacent groups [9]. There is only modest bowing in the mixed carbonato complex, but this third ligand is small and should not interfere with the two phenanthroline groups [18], and Hennig et al. [19] note distortions in some bis-phenanthroline complexes. However, variations in the NMR chemical shifts of the phenanthroline hydrogens [5b] provide evidence on distortions of these groups and indicate that it is less for phenanthroline A than B. The ^{1}H NMR chemical shifts of each phenanthroline group decrease in going from H-2 to H-9 [5b], which, for other Co(III)bis-phenanthroline complexes, was ascribed by Ito et al. [9] to π-shielding by the other phenanthroline group. For phenanthroline A, which is predicted to be near planar (Fig. 3(a)), the approximate decrease is 2.2 ppm, but for B, which is predicted to be bowed (Fig. 3(b)), it is approximately 2.7 ppm [5b], and larger than expected if π-shielding were the only factor controlling the chemical shifts [9]. A deviation from planarity of phenanthroline B should decrease its aromatic character and be reflected in the decrease in the relevant ^{1}H chemical shifts being larger for phenanthroline B than A. Chemical shifts of H-8 and 9 are lower for phenanthroline B than for phenanthroline A, but differences are small for the other positions, excepting H-2, A and B, which are close to the ligating nitrogens and the sucrose residue [5b]. These decreases in chemical shift are in addition to those due to π-shielding by the other phenanthroline as discussed by Ito et al. [9].

As shown in Fig. 1(b), little congestion is predicted between the fructose ring and phenanthroline A, which means that the conformation of the fructose hydroxymethyl group (C-1(f)–OH-1(f)) is not perturbed

and is consistent with the computed torsional angles between OH-1(f) and the hydrogens on C-1(f), as shown in Fig. 2(a), and the ^{1}H coupling constants [5a]. However, congestion between the glucose ring and phenanthroline B should influence the interaction between the latter and OH-3(g). The difference between predicted torsional angles from the semi-empirical and DFT optimizations is consistent with the H-3(g)–OH-3(g) spin–spin coupling constant in DMSO [5a], which depends on the torsional angle between the axial CH-3(g) and OH-3(g), and should be sensitive to the interaction between this OH group and phenanthroline B. The coupling constant must be very low, <2 Hz [5a], much lower than that for a freely rotating CH_2OH group, ca. 6.5 Hz [14], or that expected from the computed torsional angle of −149° from the PM3(tm) optimization which would indicate a significant coupling constant, and was originally ascribed to an apparent π-HO repulsion [5a]. However, the predicted torsional angle of −80° from the DFT optimization (Fig. 2) corresponds to a low coupling constant in accord with experiment and less repulsion between this OH group and phenanthroline B than that predicted earlier from the PM3(tm) optimization [5].

The Co(III)–oxygen bond lengths from the DFT and PM3(tm) optimizations are similar, but DFT generally gives longer Co–N bonds, and therefore lower predicted bond angles (Table 1). Both treatments predict modest deviations from a strictly octahedral symmetry at Co(III), which, as noted earlier [5b], is consistent with assignments of the CD spectra in the d–d region of mixed complexes [3b,5a] and structural evidence on other Co(III) complexes [15,16].

4. Conclusions

Except for differences in bowing of the phenanthroline rings, the predicted deprotonation of OH-2(g), rather than of OH-1(f), and the CH-3(g)–OH-3(g) torsional angle, predicted geometries from the earlier PM3(tm) optimization are not very different to those from the present ab initio treatments, and are better than the HF optimizations as regards the pyramidal geometry of OH-1(f), although DFT does not have this problem. These treatments neglect interactions with solvents, but examination of absorption, circular dichroism and NMR spectroscopy had shown that the structure does not change significantly in going from water to DMSO, despite marked differences between these solvents, especially as regards hydrogen bonding [5a,5b]. The ab initio treatments predict deprotonation of OH-2(g), consistent with the NMR evidence on the structure of the dicationic complex.

Semi-empirical methods and molecular modeling, where appropriate force fields are available [6,7,17,18], are much more economical in time than ab initio methods. This advantage is important in treating geometries, although not necessarily energies, of complex molecules [19]. Computational methods appear to be useful in predicting structures of transition metal complexes with polyol ligands where X-ray crystallography cannot be used, provided that the conclusions are supported by experimental evidence, for example from electronic and NMR spectroscopy.

Acknowledgments

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