ELSEVIER

www.elsevier.nl/locate/carres

Carbohydrate Research 329 (2000) 195–197

CARBOHYDRATE RESEARCH

Note

Complexation of sucrose with cobalt(III)bis(phenanthroline)

José Parada [a], Sergio Bunel [a,*1], Carmen Ibarra [a], Guillermo Larrazabal [a], Exequiel Moraga [a], Nicholas D. Gillitt [b], Clifford A. Bunton [b,*2]

[a] *Departamento de Quimica Inorganica y Analitica, Facultad de Ciencias Quimicas y Farmaceuticas, Universidad de Chile, Santiago, Chile*

[b] *Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA*

Received 28 April 2000; accepted 23 May 2000

Abstract

The Δ-[Co(III)bis(phenanthroline)(sucrose)]$^{3+}$ complex forms with little perturbation of the sucrose conformation, and complexation by HO-2(g) and HO-1(f). © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Sugars; Circular dichroism spectra; Complexation

Sugars, other polyols, and their amino derivatives, act as di- or tridentate ligands in ax–eq or ax–eq–ax conformations towards heavy metal ions [1]. We have examined vicinal complexes of amino or keto sugars with Co(III)bis(1,10-phenanthroline), Co(III)(phen)$_2$ [2] and the circular dichroism (CD) spectra allow assignment of configuration at Co(III) and observation of an excitonic effect confirms that two phenanthrolines are bound to Co(III) [3].

Sucrose and Co(III)(phen)$_2$(H$_2$O)(OH)$^{2+}$ in water at pH 8 generate the CD spectrum of a Δ-complex that was isolated chromatographically, as was done for other sugar complexes [2]. Its conductivity in water is that of a tricationic complex [4].

The complex retains the sign sequence of a Δ-complex in the CD spectrum in water for several weeks, whereas Co(III)(phen)$_2$(H$_2$O)$_2$ readily racemizes [5], and dilute sucrose has no CD signals in the region studied. There is no indication of formation of a Λ-complex. Some ^{1}H NMR signals have been assigned by their multiplicities and a COSY spectrum in D$_2$O. The H-1,1′(f) singlet in sucrose at 3.69 ppm (referenced to internal TSP) separates into well-defined doublets at 3.59 and 3.74 ppm (*J* 13 Hz, which is consistent with geminal coupling), although the signals in sucrose have never been separated [6]. The H-2(g) signal is shifted upfield by 0.05 ppm, and except for H-1,1′(f), multiplicities are similar to those in sucrose, including H-6,6′(g) and H-6,6′(f) [6].

Sucrose in solution adopts various conformations, including some similar to that in the solid [6–8]. The O-2(g)–O-2(f) distance in crystalline sucrose is 2.82 Å [8], the

---

[1] *Corresponding author. Fax: +56-2-7370567.

[2] *Corresponding author. Tel.: +1-805-8932605; fax: +1-805-8934120; e-mail: bunton@chem.ucsb.edu

0008-6215/00/$ - see front matter

PII: S0008-6215(00)00164-6

Co(III)–oxygen bond length is ca. 1.9 Å [9], and in octahedral Co(III) complexes an inter-oxygen distance of ca. 2.7 Å allows strain-free complexation with O-2(g) and O-1(f), despite formation of an eight-membered ring. We have seen no evidence for formation of an isolatable complex of Co(III)(phen)$_2$ with glucose, and complexation with fructose involves the pyranose form [2]. Complexation with O-1(f) readily explains the separation of the signals of H-1,1′(f). If the glucosyl residue is the bidentate ligand, it is difficult to envisage interactions that would locate the 1(f) and 1′(f) hydrogens in different environments, because coordination sites at Co(III) are fully occupied, and there is little evidence of intramolecular hydrogen bonding of sucrose in solution [7a,b]. Modelling indicates that complexation with O-1(f) and a glucose oxygen other than O-2(g) gives very strained structures.

A simulated structure of Δ-[Co(III)(phen)$_2$-(sucrose)]$^{3+}$ with complexation at OH-2(g) and OH-1(f) is shown in Fig. 1. The predicted heat of formation of the disfavored Λ-complex is less negative than that of the Δ-complex by ca. 7 kcal mol^{-1}. The sucrose ligand has a structure similar to that of free sucrose in the crystal [7c,8], but H-1(f) is closer than H-1′(f) to the face of the upper phenanthroline ring, 3.08 Å as compared with 4.17 Å, which would serve to separate the NMR signals of H-1,1′(f). Predicted bond lengths are Co–O-2(g), 2.02 Å; Co–O-1(f), 2.01 Å; the O–Co–O bond angle is 92.4° and the O-2(g)–O-1(f) distance is 2.91 Å. The phenanthroline ligands are deleted in Fig. 1(b) to make it easier to visualize the sugar residue, and sucrose Fig. 1(c), with a conformation similar to that in the crystal, was simulated with PM3 parameters that gives a structure almost identical to that from a 3-21G(*) simulation, c.f. [7c]. We note that the initial MMFF conformer search found several other conformers of sucrose [6b] whose energies were similar to that of the preferred conformer. The endocyclic fructose oxygen is in front of the plane of the paper in these structures.

Absorption and CD spectra of the complex are similar to those of other 1:1 complexes of Co(III)(phen)$_2$ [2,10]. The excitonic band at ca. 270 nm of the long-axis polarized $\pi \rightarrow \pi^*$ transition is split in the CD spectrum into components at 267 and 281 nm with the sign sequence of a Δ-Co (III) complex and with two phenanthroline groups complexed to Co(III) [3,10].

1. Experimental

The complex was prepared in water, pH 8, as described for similar complexes and isolated chromatographically (SP Sephadex C-25) with elution by NaCl or KCl, removal of water, followed by extraction of the tricationic complex in EtOH, or precipitation from the eluant with KI_3 [2]. Anal. Calcd for $[Co(phen)_2(sucrose)]Cl_3 \cdot 5H_2O$: C, 45.1; H, 5.01; Co, 6.16; N, 5.85. Found: C, 45.1; H, 4.72; Co, 6.29; N, 5.98.

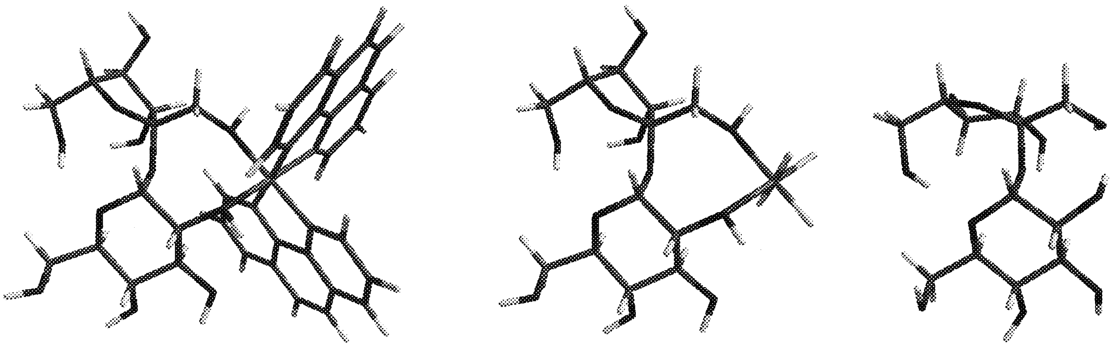

Fig. 1. Simulated structures of: (a) Δ-[Co(III)(phen)$_2$(sucrose)]$^{3+}$; (b) the complex with phenanthroline ligands removed for clarity; (c) sucrose.

The triiodide was precipitated as the dication and had the conductivity in acetone of a dicationic complex [4]. Anal. Calcd for [Co(III)(phen)$_2$(sucrose)](I$_3$)$_2$: C, 28.4; H, 2.43; Co, 3.88; N, 3.68. Found: C, 28.4; H, 2.54; Co, 3.94; N, 3.81. The CD and NMR spectra were determined in H_2O or D_2O as described [2].

Structures were simulated by a molecular mechanics MMFF conformer search, followed by the use of the semi-empirical PM3 parameters [11] (Wavefunction Spartan Plus 2.0) and perturbation and re-simulation of the structures. These simulations neglect solvation of the complex.

Acknowledgements

We acknowledge instrumental support from CEPEDEQ, Facultad de Ciencias Quimicas y Farmaceuticas, Universidad de Chile, and Professor Ines Ahumada. J.P. acknowledges support from FONDECYT, Proyecto 2970036.

References

[1] (a) S.J. Angyal, *Adv. Carbohydr. Chem. Biochem.*, 47 (1989) 1–43. (b) D.W. Whitfield, S. Stojkovski, B. Sarkar, *Coord. Chem. Rev.* 122 (1993) 171–225. (c) M. Zimmer, *Chem. Rev.* 95 (1995) 2629–2649. (d) K. Hegetschweiler, *Chem. Soc. Rev.*, 28 (1999) 239–249.

[2] S. Bunel, C. Ibarra, E. Moraga, J. Parada, A. Blasko, C. Whiddon, C.A. Bunton, *Carbohydr. Res.*, 312 (1998) 191–200 and references cited therein.

[3] K. Nakanishi, N. Berova, R.W. Woody (Eds.), *Circular Dichroism, Principles and Applications*, VCH, Cambridge, 1994.

[4] W.Y. Geary, *Coord. Chem. Rev.*, 7 (1971) 81–122.

[5] F. Basolo, R.G. Pearson, *Mechanisms of Inorganic Reactions*, Wiley, New York, 1958, pp. 264–276.

[6] (a) K. Bock, R.U. Lemieux, *Carbohydr. Res.*, 100 (1982) 63–74. (b) C.H. du Penhoat, A. Imberty, N. Roques, V. Michon, J. Mentech, G. Descotes, S. Pérez, *J. Am. Chem. Soc.*, 113 (1991) 3720–3727 and references cited therein.

[7] (a) B. Adams, L. Lerner, *J. Am. Chem. Soc.*, 114 (1992) 4827–4829. (b) L. Poppe, H. van Halbeek, *J. Am. Chem. Soc.*, 114 (1992) 1092–1094. (c) S. Bagley, M. Odelius, A. Laaksonen, G. Widmalm, *Acta. Chem. Scand.*, 48 (1994) 792–799.

[8] (a) G.M. Brown, H.A. Levy, *Acta Crystallogr., Sect. B*, 29 (1973) 790–797. (b) J.C. Hanson, L.C. Sieker, L.H. Jensen, *Acta Crystallogr., Sect. B*, 29 (1973) 797–808.

[9] R. D. Gillard, N.C. Payne, G. B. Robertson, *J. Chem. Soc. A*, (1970) 2579–2586.

[10] (a) S.F. Mason, *Inorg. Chim. Acta Rev.*, 2 (1968) 89–109. (b) B.E. Douglas, T. Yasui, *Inorg. Chem.*, 10 (1971) 97–102.

[11] (a) J.J.P. Stewart, *J. Comput. Chem.*, 10 (1989) 209–2820. (b) J.J.P. Stewart, *J. Comput. Chem.*, 11 (1990) 543–544.