CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Silicon–Chelation in Aqueous and Non-Aqueous Media:
The Furanoidic-Diol Approach

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In our work, a recent publication of the Lambert group (J. B. Lambert, G. Lu, S. R. Singer, V. M. Kolb, *J. Am. Chem. Soc.* **2004**, *126*, 9611 – 9625) is frequently cited.

The work deals with silicon chelation by common mono- and disaccharides in aqueous solution of pH 11.7.

To detect glycose/silicate species, silicate solutions have been added to aqueous alkaline solutions of ribose and other common glycoses at pH 11.7. New signals are interpreted as stemming from Si-bonded furanoses. Since these signals are weak and badly resolved, assignment to carbon atoms is carried out with the expectation that the signal of a carbon atom that bears a silicon-chelating oxygen atom exhibits a typical down-field shift of about 4 ppm ("ß effect"). This value was determined from a DEPT spectrum showing both free and Si-bonded anhydroerythritol. This calibration procedure, however, went completely wrong since the C1/4 and C2/3 signals of both free and Si-bonded AnEryt were confused by erroneously switching the CH and CH_2 coordinate of the DEPT spectrum. This wrong calibration causes the signal assignment of sugars to be arbitrary. This is shown for ribose in Figure 1. Ribose was chosen, since it is the only sugar which is discussed in detail in Lambert's work.

Using the stepwise evaluation based on 2D assignments described in the main text, the result is different. Lambert's ß*f*-C2 turns to a*f*-C4, while Lambert's ß*f*-C1 (which is significantly weaker in our spectrum than in his) possibly stems from small amounts of ß*f*-2,3 ligation. There is thus no indication for ß-Rib*f*-1,2 chelation which, moreover, can be ruled out on the basis of DFT calculations. It remains completely unclear why Lambert concludes that only *cis*-furanoses can act as silicon ligands, but detects ß-Rib*f*-1,2 binding, i.e. the binding of a *trans*-furanose, in the discussion of his spectra.

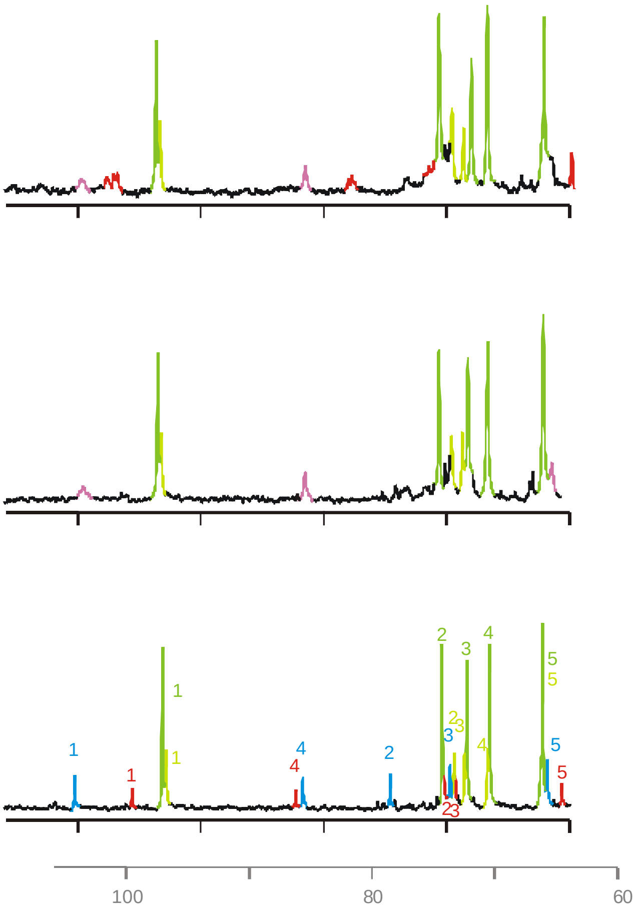

Figure 1. Additions to Fig. 17d–f of the main text: The d scale used by Lambert is somewhat different from ours and is added in grey. In the top spectrum, Lambert’s assignments are added in grey.