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A Novel Mode of Specific Interaction between $CuCl_2$ and D-Fructose in Dimethyl Sulfoxide-Water Systems

Koji ARAKI and Shinsaku SHIRAISHI
Institute of Industrial Science, The University of Tokyo,
7-22-1 Roppongi, Minato-ku, Tokyo 106

The interaction of $CuCl_2$ with D-fructose in a dimethyl-d_6 sulfoxide(DMSO)-D_2O mixture showed a large solvent effect with $CuCl_2$ being found to interact specifically with the C4 and C5 hydroxyl groups of β-pyranose when the DMSO content was higher than 75% in the mixture.

Trace amounts of transition metal show variety of physiological activities. However, relatively little is known as to anomer- and site-specificities of the interactions between biologically-important transition metals and carbohydrates in solutions, though the metal sequestering ability of carbohydrates has been attracting considerable interest.[1)] Here, we studied the specific interactions between $CuCl_2$ and D-fructose in D_2O-dimethyl-d_6 sulfoxide(DMSO) by ^{13}C-NMR spectrometry,[2)] which showed a drastic solvent-induced change in their mode of interactions. D-Fructose(0.5 mol dm^{-3}) was dissolved in a D_2O-DMSO-d_6 solution, and ^{13}C-NMR spectra were recorded on a JEOL GX-270 operated at 67.8 MHz at 27.0 °C.[2,3)]

^{13}C-NMR spectra of D-fructose in D_2O-DMSO-d_6 systems showed well resolved signals for most of the carbons of three major anomers, β-pyranose(βP), and β- and α-furanoses(βF and αF, respectively). The equilibrium anomer composition determined from the relative intensities of the anomeric carbon(C2) signals suffered large solvent effect, and the amounts of βF and αF increased at the expense of βP as the DMSO-d_6 content was increased (Fig.1).[3)]

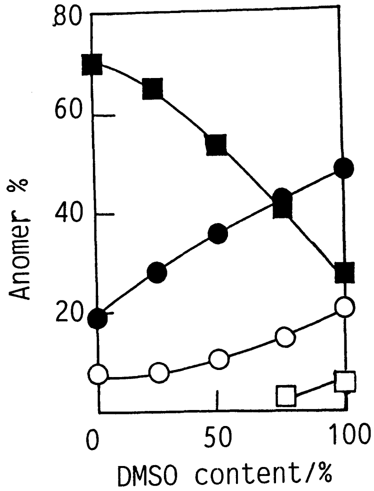

Fig. 1. The Anomer Composition of D-Fructose(0.5 mol dm^{-3}) in D_2O-DMSO-d_6 at 27 °C. (■) βP, (□) αP, (●) βF, and (○) αF.

To the solutions of D-fructose(0.5 mol dm^{-3}) in D_2O-DMSO-d_6 after attaining anomer equilibrium, a small amount of $CuCl_2$ ($0.8\text{-}3\times10^{-2}$ mol dm^{-3}) was added and ^{13}C-NMR spectra of the solutions were measured. In the case of D_2O solvent, addition of $CuCl_2$ resulted in a non-specific broadening of the signals, though intensities of the anomeric carbon signals decreased slightly more than those of other signals. The hydroxyl groups at these carbons are the part of either a *cis* diol of furanoses or an *ax-eq-ax* triol of pyranose, which are known to interact preferentially with $CuCl_2$ and other metal ions in water.[1,2] While, in the case of DMSO-d_6, addition of $CuCl_2$ caused specific broadening of the C4 and C5 signals of βP(βP4 and βP5, respectively), and these signals practically disappeared upon addition of more than 1.6×10^{-2} mol dm^{-3} of $CuCl_2$ though other signals of the βP were still observed(Fig. 2). The result clearly indicates that Cu(II) interacts specifically with the C4 and C5 hydroxyl groups of βP in DMSO-d_6, though this anomer comprised only 30% of D-fructose. These hydroxyl groups do not conform to the *ax-eq-ax* hydroxyl sequence nor do they include the anomeric hydroxyl group which is more acidic compared to other hydroxyl groups. As the *ax-eq-ax* sequence of βP and *cis*-diol of furanoses including the anomeric hydroxyl group also exist in the solution, the selective interaction of Cu(II) toward the hydroxyl groups at βP4 and βP5 is not a common mode of interaction. No explanation for the observed specificity was obtained from the ESR and electronic spectra of a $CuCl_2$-D-fructose solution.[4]

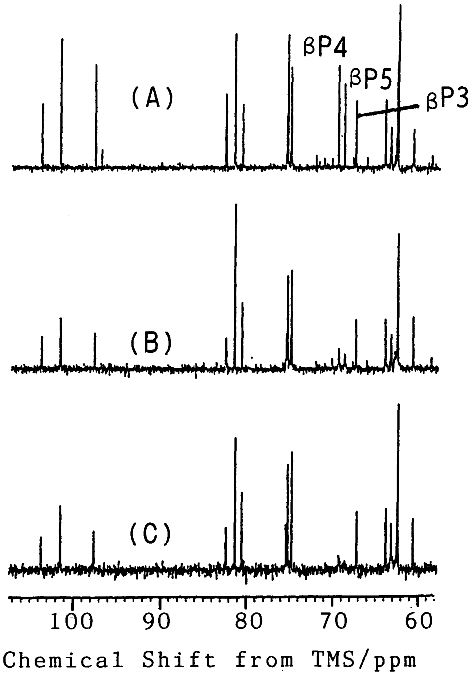

Fig. 2. ^{13}C-NMR Spectra of D-Fructose (0.5 mol dm^{-3}) in the Presence of (A) 0, (B) 13, and (C) 29 x 10^{-3} mol dm^{-3} of $CuCl_2$ in DMSO-d_6.

When the DMSO-d_6 content was decreased to 75%, the $CuCl_2$-induced broadening of the βP4 and βP5 became less evident. Further decrease in DMSO-d_6 content suppressed the specific broadening of these signals, and, instead, the $CuCl_2$-induced spectral change became similar to those in D_2O. Thus, the specificity of the $CuCl_2$-D-fructose interaction is shown to be sensitive to the nature of solvents. To our knowledge, little is known as to the solvent effect on the mode of specific interaction between transition metals and carbohydrates.

References

1) S.J.Angal, Chem.Soc.Rev., 9, 415(1980); J.Briggs, P.Finchi, M.C.Matulewicz, and H.Weigel, Carbohydr.Res., 97, 181(1981); K.Araki, M.Sakuma, and S.Shiraishi, Bull.Chem.Soc.Jpn., 57, 997(1984); H.A.Tajmir-Riahi, J.Inorg. Biochem., 27, 65(1986); M.Izumi, Carbohydr.Res., 170, 19 (1987). 2) K.Araki, S.Shiraishi, Carbohydr.Res., 148, 121 (1986). 3)Sample solutions were kept at room temperature for at least a day in the case of D_2O or two weeks in the case of DMSO-d_6 prior to the measurements in order to attain anomer equilibrium.; B.Schneider, F.W.Lichtenthaler, G.Steinle, and H.Schiweck, Liebigs Ann.Chem., 1985, 2443. 4) $A_{\parallel}$=128 G, $g_{\parallel}$=2.372, $g_{\perp}$=2.083 for a $CuCl_2$(0.01 mol dm^{-3})-D-fructose(0.1 mol dm^{-3})/DMSO solution at 77 K. Upon addition of D-fructose to a $CuCl_2$/DMSO solution, absorbance of the solution at 300-400 nm presumably due to a $[Cu(dmso)Cl_3]^-$ or $[Cu(dmso)_3Cl]^+$ species was decreased.; M.Elleb, J.Meullemeestre, M-J.Schwing-Well, and F.Vierling, Inorg. Chem.,21, 1477(1982).

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