Synthesis and optical sensing properties of a boronic acid appended rhenium(I) complex for sugar

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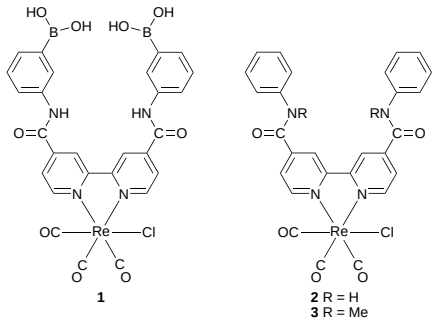
A rhenium(I) complex with boronic acid pendant is synthesized and characterized; the complex is shown to exhibit pH dependent electronic absorption characteristics; the photophysical properties and sugar sensing behaviour are also investigated.

Boronic acids, which have been known to form covalently bonded complexes with diols in aqueous system, have attracted a great deal of attention as an interactive tool for sugar recognition.[1,2] Much attention has been focused on the application of boronic acids with organic backbones as fluorescent chemosensors for sugars.[2] Although there were reports on the synthesis of iron(II) complexes with boronic acid-containing ligands, they were mainly confined to those of electrochemical[3] and circular dichroism (CD) spectroscopic studies.[4] There has been, to the best of our knowledge, no report of transition metal coordination/organometallic compounds of this kind employed as absorbance or luminescence probes. With our recent interest in the utilization of metal-to-ligand charge transfer (MLCT) excited states as spectrochemical and luminescence probes as well as in the study of host–guest interactions,[5] an attempt to extend our attention to sugar recognition was pursued. Herein are reported the synthesis and luminescence behaviour of a rhenium(I) complex **1** with boronic acid pendant. The changes in the electronic absorption and luminescence properties induced by the presence of various types of mono- and di-saccharides have been investigated and the binding constants determined using spectrochemical methods. Complexes **2** and **3** have also been synthesized for comparative spectrochemical studies. All complexes **1**–**3** have been characterized by ^{1}H NMR, IR spectroscopy and positive FAB mass spectrometry, and gave satisfactory elemental analyses.†



The UV–VIS spectrum of complex **1** shows a low energy absorption band at *ca*. 370 nm, typical of the MLCT transition of rhenium(I) diimines.[6] Excitation of an aqueous solution of **1** at λ = 430 nm showed an intense luminescence at *ca.* 620 nm, which is typical of the phosphorescence derived from the triplet rhenium-to-diimine metal-to-ligand charge transfer (^{3}MLCT) excited state.[6] Both the MLCT absorption and emission bands in Me_2SO–H_2O (1 : 1 v/v) were found to show a blue shift in energy as the pH[7] was increased. Besides the blue shift from *ca.* 670 nm in acidic medium to *ca.* 620 nm in alkaline medium was observed in the emission maxima, a rise in emission intensity was found to occur as the pH increased. The pK_a of **1** was found to be 5.9, which we attributed to hydroxide capture by the boronic acid group. A typical pK_a of *ca.* 9 was reported for phenylboronic acid in aqueous solution,[8] quite different from the medium used in the present system. It is believed that coordination of the ligand to the metal centre would stabilize the boronate pendant and hence lowered its pK_a value. A similar pK_a has been obtained in a separate experiment using a universal phosphate–citrate buffer with constant ionic strength.[9] In order to choose an optimum working pH for the sugar binding studies, the absorption spectra of **1** at pH 5.5–10.5 both in the absence and in the presence of 0.2 mol dm^{-3} D-fructose were measured. D-Fructose was chosen as it has previously been reported to show the largest spectral change among the various types of saccharides studied.[1,2,8] The largest spectral change induced by D-fructose was observed at pH 8.3 for **1**, which was thus employed for our subsequent measurements.

The UV–VIS spectral traces of **1** in glycine–NaOH buffer[10] at pH 8.3 in the presence of various amounts of added D-fructose showed an isosbestic point at *ca*. 350 nm. Fig. 1 depicts the titration curve of **1** with different sugar substrates. D-Fructose was found to induce the largest spectral change of **1**. By applying the equation $A_0/(A_0 - A) = (\varepsilon_0/\varepsilon_0 - \varepsilon)[(1/K[S]) + 1]$[11] and a plot of $A_0/(A_0 - A)$ *vs.* $[S]^{-1}$, the stability constants K could be obtained from the ratio slope/*y*-intercept, where A_0 and A are the respective absorbances at 376 nm in the absence and in the presence of saccharide S with concentration [S], and ε_0 and ε are the absorption coefficients for the free and sugar-bound rhenium(I) complex, respectively. The stability constants for 1 : 1 complexation in glycine–NaOH buffer : Me_2SO (1 : 1 v/v) are: D-fructose (log K = 2.40); L-arabinose (log K = 1.56); D-galactose (log K = 1.54); D-mannose (log K = 1.29); D-glucose (log K = 1.18); maltose (log K = 0.91); lactose (log K = −0.37). It was found that D-fructose gives the largest log K value. Similar trends have also been observed in the related organic systems.[1,2]

The selective preference of **1** for mono- over di-saccharides has been attributed to the covalent bonding interaction of the hydroxyl groups on the saccharides to the boronate ions; the

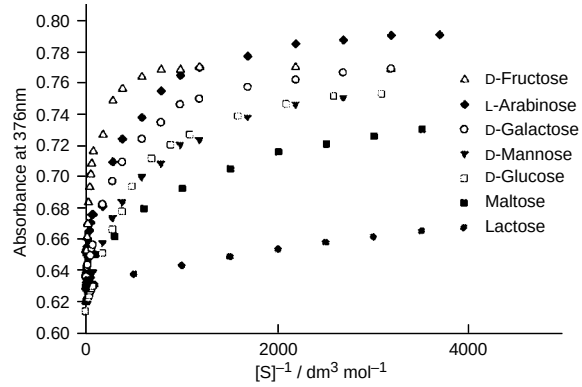


Fig. 1 Plot of absorbance of **1** (0.1 mM) at 376 nm in glycine–NaOH buffer : Me_2SO (1 : 1 v/v) at pH 8.3 as a function of sugar concentration for selected sugars

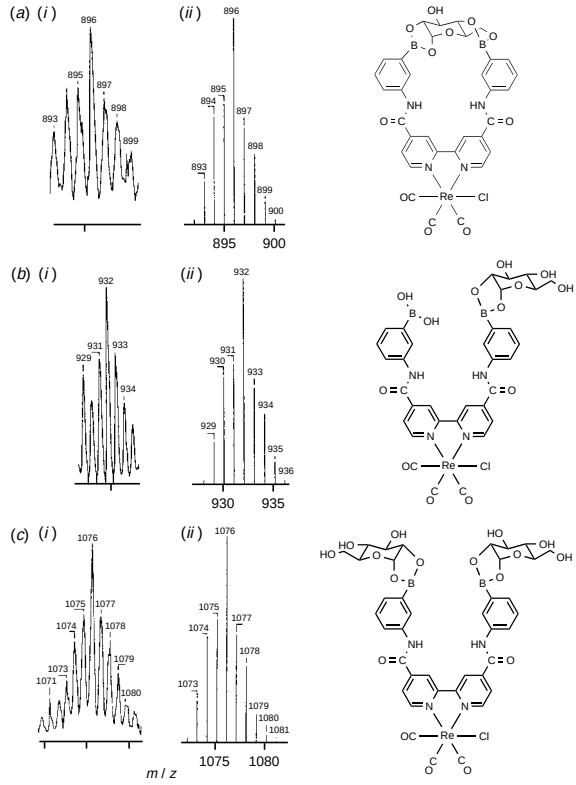


Fig. 2 Expanded ion cluster from the negative FAB mass spectrum of a buffered solution containing **1** and D-glucose. (*a*) (*i*) *m*/*z* 896, (*ii*) simulated isotope pattern for $ReB_2C_{33}ClH_{24}N_4O_{11}$; (*b*) (*i*) *m*/*z* 932, (*ii*) simulated isotope pattern for $ReB_2C_{33}ClH_{28}N_4O_{13}$; (*c*) (*i*) *m*/*z* 1076, (*ii*) simulated isotope pattern for $ReB_2C_{39}ClH_{36}N_4O_{17}$.

selectivity of which is controlled by the size of cavity as governed by the two boronate groups. The existence of the 1:1 complex of **1** with D-glucose was established by negative FAB mass spectrometry. Fig. 2 shows the expanded ion clusters observed in the mass spectrum of a mixture of **1** and D-glucose. The binding of monosaccharides, like D-glucose, to **1** gave both 1 : 1 cyclic and 1 : 1 non-cyclic bound species at low saccharide concentrations. At high concentration of saccharides, apart from the 1 : 1 complexes, the 1 : 2 complex also exists. The site of binding has also been confirmed by related studies using the analogous complex **2** in which the boronic acid groups were absent as a control. Unlike **1**, addition of D-fructose to **2** at pH 8.3 induces no spectral change, indicative of the importance of the boronic acid pendants in the binding action. However, as the pH is increased to 12.1, both **1** and **2** showed a similar increase in the absorbance upon addition of D-fructose with the absence of isosbestic points in the electronic absorption spectral traces. It is likely that under such high pH conditions, deprotonation of the amide group would occur to bind the saccharides. Deprotonation of the amido proton has been reported to occur at high pH. Organic amides such as benzanilide and *p*-bromobenzanilide showed pK_a values of 16.53 and 15.73, respectively;[12] the pK_a values are dependent on the electronic factors with electron withdrawing substituents stabilizing the imide anion, and lowering the pK_a value. The emissive behaviour of **1** and **2** is similar, each showing an emission maximum at *ca*. 620 nm, the intensity of which increased significantly upon addition of sugars. Similar changes in the emission behaviour were not observed for **1** and **2** at pH 8.3. In order to investigate the behaviour of complex **2** under high pH condition, complex **3** was prepared in which the amido protons were replaced by methyl substituents. Unlike complexes **1** and **2**, the addition of D-fructose to **3** at pH 12.1 induces no spectral change. It is worth noting that the role played by the amido group in sugar binding at high pH values should not be overlooked. Work is in progress to explore the potential of such binding properties.

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Footnotes and References

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† **1**: ^{1}H NMR [300 MHz, $(CD_3)_2SO$, 298 K, relative to TMS]: δ 7.40 (q, 2 H, aryl), 7.63 (d, 2 H, aryl), 7.93 (d, 2 H, aryl), 8.07 (s, 2 H, aryl), 8.13 (s, 4 H, OH), 8.21 (dd, 2 H, bipyridyl), 9.24 (dd, 2 H, bipyridyl), 9.26 (s, 2 H, bipyridyl), 10.83 (s, 2 H, amido). **2**: ^{1}H NMR [300 MHz, $(CD_3)_2SO$, 298 K, relative to TMS]: δ 7.20 (t, 2 H, aryl), 7.43 (t, 4 H, aryl), 7.79 (d, 4 H, aryl), 8.18 (dd, 2 H, bipyridyl), 9.25 (dd, 2 H, bipyridyl), 9.26 (s, 2 H, bipyridyl), 10.87 (s, 2 H, amido). **3**: ^{1}H NMR [300 MHz, $(CD_3)_2SO$, 298 K, relative to TMS): δ 3.33 (s, 6 H, Me), 7.17 (m, 10 H, aryl), 7.32 (dd, 2 H, bipyridyl), 8.32 (s, 2 H, bipyridyl), 8.74 (dd, 2 H, bipyridyl). Positive FABMS: ion cluster at *m*/*z* 725 [M^+].

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