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Novel Keto-enol Tautomerism in 1,3,5-trihydroxybenzene Systems

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We report a new synthesis of the water-soluble compound 1,3,5-trihydroxy-2,4,6-trimethylsulfonic acid (1), which exists in two tautomeric forms (60:40::enol%:keto%) and can be used as a proton conductor. Quantum chemical calculations show the importance of intramolecular hydrogen bonding and the presence of implicit MeOH solvent on the relative stabilities of the tautomers. 1 complexes with lanthanides through its sulfonato groups and forms a layered cage-like structure with one intramolecular and two intermolecular hydrogen bonds.

In supramolecular chemistry, water-soluble sulfonate compounds of calixarenes are of particular interest for their use as constituents of metal ion complexes[1] and as precursors for artificial receptors of organic molecules and ions. [2] Sodium *p*-sulfonatocalix[4,5]arenes, for example, complex with organic molecules (e.g., 18-crown-6, pyridine) and with inorganic metals (e.g., main group and transition metals, lanthanides) in aqueous solution. The bowl shape of this macrocycle allows construction of a diverse range of inclusion complexes as well as discrete spherical and tubular frameworks[1d,3] Atwood and co-workers have reported the complexation of *p*-sulfonato-calix[4]arene with the lanthanide metal ions Yb^{3+} and Tb^{3+}. The resultant ytterbium(III) coordination complex has a bilayer-type arrangement with the central metal ion bonded directly to one of the sulfonato groups and H_2O molecules in the bowl cavity[1c,3] When the metal ion is terbium(III), the sulfonato group complexes with $[Tb(H_2O)_8]^{3+}$ ions. In this case, the oxygens of the sulfonato group hydrogen bond with the closest aqua groups of $[Tb(H_2O)_8]^{3+}$ and form a bilayer complex.[1h] More recently, Dalgarno and co-workers have shown complexation of *p*-sulfonatocalix[4]arene with praseodymium(III) nitrate salts and perchlorate salts to yield 3-D coordination polymers and discrete entities, respectively.[6] In all cases, the frameworks are held together through π-π stacking, coordination-bonding and hydrogen-bonding (H-bonding) interactions.

With respect to artificial receptors, water-soluble metal-organic sulfonate complexes have important applications in the area of proton exchange across membranes.[4] For example, Hurd and co-workers and Kim *et al.* have reported the proton-conducting metal organic framework 2 (β-PCMOF2) of the trisodium salt of 2,4,6-trihdroxy-1,3,5-benzenetrisulfonate. This complex of β-PCMOF2 has a honeycomb-like network structure with pores of ~ 6 Å, created by the binding of Na ions to two hydroxyl and six oxygen atoms of the sulfonate groups. The presence of the sulfonate oxygen atoms in the pores enhances the efficiency of the proton transfer pathway. That the cavity of β-PCMOF2 is doped with 1*H*-1,2,4-triazole (Tz) guests also makes the transfer between proton conductors more efficient.[4] In contrast, most of the other reported proton conductors, such as nafion,[5] conduct protons based on the humidity.

Inspired by the structural and functional diversity of sulfonato complexes, we investigated the synthesis of related water-soluble complexes. Specifically, we report an improved synthesis of the water-soluble tri-sulfonated compound, 1,3,5-trihydroxy-2,4,6-trimethylsulfonic acid, compound **1** (Scheme 1), and its complexation with lanthanide ions. The synthesis of **1** involves a reflux reaction of a mixture of 1,3,5-trihydroxybenzene, aqueous sodium sulfite and paraformeldehyde at 90-95 ^{0}C for a period of four hours. The resultant product is neutralized with 1M HCl and washed with acetone to obtain compound **1**.[7] Compound **1** is a hexasubstituted benzene[8,9] with three hydroxyl groups at positions 1,3,5 and three methyl sulfonic acid groups at positions 2,4,6 of the aromatic ring (Scheme 1). Compared to the traditional method by Hurd et al. (24 h),[7] this new method is much shorter (4-5 h) and provides a high yield (~ 98%).

Compound **1** is highly soluble in aqueous solution (greater than 0.6 M). Moreover, solution studies (low temperature ^{1}H and ^{13}C NMR) of compound **1** in methanol proved to be intriguing. The ^{13}C spectrum was rather difficult to assign and

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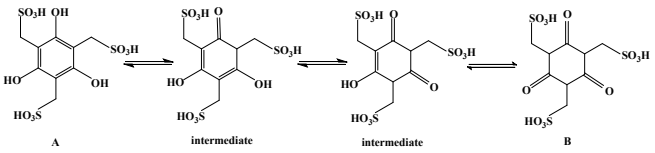
suggested the presence of more than one species in solution (SI). To further investigate, we conducted ^{1}H-NMR in 95% H_2O:5% D_2O, ^{13}C-NMR in D_2O and solid-state ^{13}C-NMR studies. Both ^{13}C-NMR studies indicated that compound **1** exists in two forms or tautomers, namely, 1,3,5-trihydroxy 2,4,6-trimethylsulfonic acid, the phenolic tautomer A, and 1,3,5-cyclohexanetrione 2,4,6-trimethylsulfonic acid, the ketonic tautomer B[10-14] (Scheme 1). To our knowledge, the analogous tautomeric equilibrium is not observed experimentally for substituted 1,3,5-trihydroxybenzenes in H_2O.



Scheme 1. Schematic representation of the tautomerization process observed in solution of water-soluble 1,3,5-trihydroxy-2,4,6-trimethylsulfonic acid, **1**.

The comparison of the two ^{13}C NMR spectra of **1** (SI) demonstrates an excellent agreement between the two sets of peak positions. The spectra show one singlet for the CH_2 carbons of structure A in Scheme 1 and one singlet for those of structure B at ~ 46.5 ppm (peak nos. 3,6), one singlet for the carbons on the aromatic ring of tautomer A at ~ 101.8 ppm (peak no. 2), one singlet for the carbons of the aromatic ring connected to the –OH group at ~ 154.1 ppm (peak no. 1), and one singlet for the carbons of the C=O group of cyclohexane at ~ 189.6 ppm (peak no. 4). The expected peak at ~61 ppm associated with the CH carbons of tautomer B is not obvious, perhaps due to the interchange among the four potential structures illustrated in Scheme 2. There is a possible impurity signal at ~ 18.5 ppm.

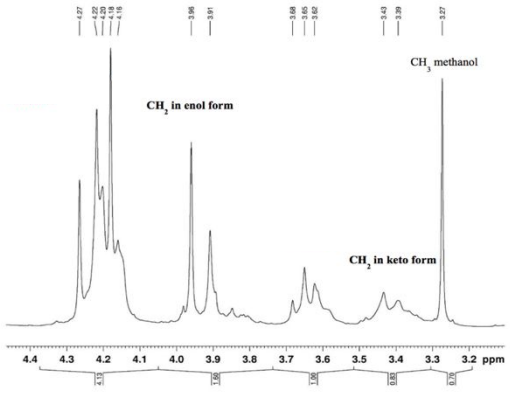


Figure 1. The spectrum of ^{1}H NMR at 279.9 K of **1** in 95% H_2O:5% D_2O.

The ^{1}H NMR spectrum, thus, shows the presence of both keto and enol forms when the reaction is in equilibrium (Figure 1). The integration of the area of the peak corresponds to the concentration of keto and enol forms. The relative percentages of the enol and keto forms in solution are calculated from the ratio of the resonance characteristic for each form and the ratio is also associated with the equilibrium constant, K_e

$$K_e = \frac{\%enol}{\%keto} = \frac{(CH2\ peak\ area\ of\ enol\ form)}{(CH2\ peak\ area\ of\ keto\ form)} qw$$

In Figure 1, the methylene protons (–CH_2–) are used to obtain K_e (SI). The ^{1}H-NMR spectrum of **1** in 95%H_2O:5% D_2O at 279.9 K provides a value of K_e of 1.93 corresponding to a 60:40::enol%:keto%, showing a preference for the enol form.

Thermal gravimetric analysis (TGA) (see SI) of compound **1** shows that the dehydration occurs at a lower temperature of 100.8 °C (obsv. 10.53%, calc. 11.67%). The area between 100.8 °C – 326.5 °C suggests possible loss of some solvent molecules along with the decomposition of the structure most likely through the loss of SO_2 or SO_3 (obsv. 38.76%, calc. 43.58%).

Quantum chemical calculations were carried out to explore the intramolecular H-bonding interactions within and relative energetics of the tautomers. To assess the effect of the methylsulfonato substituents on the energetics, PBE0/aug-cc-pVDZ fully optimized structures, in the presence and absence of implicit MeOH solvent, were obtained for the fully keto and fully enol forms of 1,3,5-trihydroxybenzene as well as of compound **1**. The ωB97X-D/aug-cc-pVTZ//PBE0/cc-pVDZ most ergonically favorable equilibrium structures identified, from a variety of starting structures (see computational details in SI), are depicted in Figure 2. Two structures are displayed for B because the preferred gas- and solution-phase structures differ. Indeed, B1 is not a minimum on the potential energy surface when solvent effects are included. A distorted boat conformation is adopted by all three keto tautomers. The chair conformers are either less favored ergonically or rearrange to the boat.

For compound 1, the preferred structures are those that exhibit a larger number of intramolecular H-bonded rings or larger rings. For all of these structures, AIM analysis finds bond critical points for all of the individual H-bonds and, with the exception of the 12-membered ring, ring critical points for the H-bonded rings. The A and B2 configurations have three 7-membered rings, whereas the B1 configuration has one 12-membered ring. The rings are formed by S=O···H-OC (A), S=O···H-OS (B1) or C=O···H-OS (B2) H-bonds (Figure 2). For both A and B, there are minimal fluctuations in relative enthalpies and free energies due to rotation of the hydrogen atom of the sulfonato (A or B**)** or hydroxyl (A) groups provided the intramolecular H-bonded network is not disrupted.

The effect on the energetics due to the disruption in H-bonding is best illustrated by form B. When comparing B1 and B2, B2 has gas-phase ΔH (ΔG) values of 42 (12) kJ/mol. The large increase in entropy as the H-bonded ring size is reduced from 12 to 7 (641 vs. 704 J/(mol·K) makes the ΔH and TΔS terms comparable in magniFtude (T=298K, Figure 2). Similarly, as the 7-membered rings are disrupted to one or no rings, the ΔH (ΔG) values increase by 59 (29) and 76 (40) kJ/mol, respectively. The data for the systems with three 7-membered rings and with no rings allows us to estimate average intramolecular H-bond strengths, while minimizing structural differences. Assigning all of the enthalpy loss between the systems to the loss of H-bonding yields an upper limit of ~11 kJ/mol per bond for the strength of the intramolecular H-bonds in B2.

In both sets of tautomers, the aromatic hydroxyl compounds are more stable than the ketone analogues (Figure 2). Perhaps surprisingly given the experimental observations, adding methylsufonato substituents to 1,3,5-

trihydroxybenzene inherently destabilizes the keto tautomer relative to the enol. In the gas phase, upon substitution the preference for the enol increases by 60 kJ/mol for B1 and 72 kJ/mol for B2. Although the enthalpic contribution to this change in relative free energy is larger, the entropic contribution favors the keto form of 1,3,5-trihydroxybenzene but the enol form of **1**. Accounting for implicit solvent effects reduces the enhanced preference for the enol form upon substitution to 31 kJ/mol. Individually, under these conditions, the keto tautomer of 1,3,5-trihydroxybenzene is destabilized relative to the enol, whereas the keto tautomer of **1** is stabilized. The latter result is due solely to enthalpic contributions as A and B2, both of which have three 7-membered H-bonded rings, have entropies within 1 J/(mol·K) despite their different connectivities and geometries.

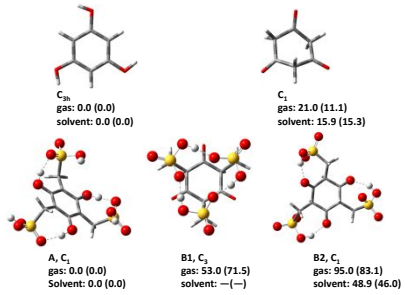


Figure 2. PBE0/aug-cc-pVDZ fully optimized structures of the enol (left) and keto (right) tautomers of 1,3,5-trihydroxy-benzene (top) and compound **1** (bottom). Intramolecular H-bonding interactions are designated with dashed lines. Molecular point groups and ωB97X-D/aug-cc-pVTZ//PBE0/aug-cc-pVDZ relative enthalpies and free energies (in parentheses) in kJ/mol are given.

Consistent with the above thermodynamic data, in the gas phase the H-bond O···O distances lengthen from the A to B2 structures by at least 0.06 Å (2.66-2.70 Å vs. ~2.76 Å, SI). Also, the O-H···O angles decrease by at least 11° (162-165° vs. 151°). On the basis of these criteria, the intramolecular H-bonds are stronger in A than in B2, a result that enhances the enthalpic (and ergonic) preference for A. In contrast, the gas-phase O···O distances (1.65 Å) and O-H···O angles (170°) for B1 demonstrate that it has the strongest H-bonds of the three systems. This result correlates with the trend in stability for B1 and B2 but not for B1 and A. Accounting for implicit solvent effects reverses the structural differences for A and B2. Specifically, for B2 the O···O distances and O-H···O angles shorten by 0.09 Å and increase by 5-10°, respectively. For A these bonds and angles lengthen by 0.06-0.09 Å and decrease by 5°, respectively. Overall, including solvent effects in the calculations strengthens the intramolecular H-bonds of B2 and weakens the H-bonds of A such that the former H-bonds are now stronger than the latter.

In assessing whether strengthening intramolecular H-bonding interactions in B competes with loss of aromaticity for this tautomer, we note that 1) H-bond strengths for neutral compounds generally range from 8-60 kJ/mol,[15] with intramolecular interactions weaker than their intermolecular counterparts; and 2) aromatic stabilization of benzene is generally considered to be ~140-150 kJ/mol.[16] Even assuming the stability contributed by intramolecular H-bonding is 30 kJ/mol per H-bond, the three such bonds in species A and B2 would not contribute sufficient stability to counter the loss of aromaticity. On the other hand, with B1 exhibiting four intramolecular H-bonds, the extra H-bond and stronger H-bonds for B1 compared to B2 could largely account for the observed 42 kJ/mol difference in the gas-phase enthalpies of these two species.

Clearly, the remaining 46 kJ/mol difference in free energy between the A and B2 tautomers in the presence of implicit MeOH solvent (Figure 2) is by far too large to account for the observed tautomeric equilibrium in MeOH solution. The much smaller 15.3 kJ/mol difference in free energy between 1,3,5-trihydroxybenzene and 1,3,5-cyclohexanetrione still exceeds the 10 kJ.mol limit required to establish the equilibrium. In particular, the calculations imply that although intramolecular H-bonding is important in stabilizing the A and B tautomers, we anticipate that explicit solute-solvent interactions are the dominant factor accounting for the tautomerism exhibited by **1** and not exhibited by 1,3,5-trihydroxybenzene.

In addition to the synthesis and characterization of compound **1,** we also investigated the syntheses of metal-organic complexes of compound **1** with lanthanide salts. Stoichiometric ratios of compound **1** and lanthanide nitrates were mixed in methanol, ethanol, and water solvents and the pH was adjusted to 1. Note that the lanthanide cations easily hydrolyze to form hydroxyl lanthanide, leading to the formation of insoluble hydroxides. Therefore, control of the pH of the lanthanide salt solution is crucial for molecular self-assembly and subsequent crystallization. Crystallization conditions were monitored over several days and crystals suitable for X-ray diffraction studies were obtained exclusively in methanol, possibly due to the intermediate polarity. Single crystals of complexes of compound **1** with Sm, Eu, La, Ho, Nd and Tb were studied and were found to be isostructural. Thus, herein we report and discuss the structure of only two complexes, namely **1·Eu** and **1·Sm** from the group. The crystals of **1·Eu** and **1·Sm** are isomorphous and were refined in the monoclinic space group $P2_1/n$. Compound **1** predominantly adopts the tautomer A conformation in complexes **1·Eu** and **1·Sm** and it crystallises in a 1:1 ratio with Eu/Sm (SI). However, in both structures one of the phenolic oxygen atoms has anomalously large atomic displacement parameters, which we consider evidence for dynamic disorder between tautomers A and B. This phenolic group is the only one involved in a strong intramolecular hydrogen bond, which provides a pathway through which hydrogen exchange can occur in the solid state.

The asymmetric unit consists of two Eu/Sm centers and two molecules of **1.** In each molecule (**1**), the three sulfonate groups are positioned in the same direction creating a tripodal orientation (Figure 3). However, individual units of **1** are positioned anti-parallel resulting in three sulfonate and a Sm/Eu center above the plane and three sulfonates and a Sm/Eu center below the plane. The carbon to oxygen (of the hydroxyl group) bond length of ~1.35 Å in both complexes indicates the presence of the enolic (C—OH) versus the ketonic form. The extended structure of **1·Eu** and **1·Sm** forms sheets which stack on top of each other. The layers stack to form a series of π-stacking interactions between aromatic regions of **1** with a

centroid···centroid distance of 3.50 Å (Figure 3). Further investigation of the extended structure reveals the presence of a second layer which is offset to the original layer and is positioned diagonally (see SI). Within the asymmetric unit, two sulfonato groups of neighbouring molecules of **1** coordinate with a single metal centre. Interestingly, the metal centres forms a connection between individual units of **1** forming a layered network. Each metal centre has an octahedral geometry and coordinates with two sulfonatos, one methanol and five water molecules. Solvent molecules of adjacent units are within hydrogen-bonded distances. An extended network shows a criss-cross of layers held together by metal centres.

Figure 3. A) Representation of part of the asymmetric unit observed in **1·Eu**. B)

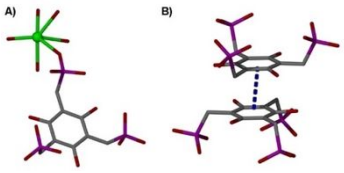


Illustration of the π-stacking interactions (blue dashed line) present between neighbouring layers in the extended/packing structure of **1·Eu**. Hydrogen atoms have been omitted for clarity. Colour codes: C: grey, O: red, Eu: green, S: magenta/dark pink.

In summary, we report a more convenient and easier method of synthesis for compound **1.** The proposed method has fewer synthetic steps compared to those tried earlier.[4c] The NMR studies reveal a novel tautomeric conformational change and the presence of both keto and enol forms of compound **1**. In addition, we report, for the first time, the synthesis and structures of lanthanide complexes of compound **1**. All lanthanide (Sm, Eu, La, Ho, Nd and Tb) complexes of compound **1** were exclusively isolated from methanol at pH 1. All of the lanthanide complexes of **1** are isostructural (hence, only **1.Eu** and **1.Sm** are reported) and self-assemble into a bilayer-type arrangement with π-stacking between adjacent aromatic layers.

The gas-phase quantum chemical calculations show that the keto tautomer is inherently destabilized relative to the enol tautomer upon substitution of methylsulfonato groups on the aryl ring of 1,3,5-trihydroxybenzene. Including implicit solvent effects in the calculations does strengthen the intramolecular H-bonds in B compared to A and diminishes the preference for the enol tautomer of **1**, as opposed to the enol tautomer of the parent compound, but not to a sufficient extent to offset the loss of aromaticity. Ultimately, the calculations disclose the need to examine explicit solute-solvent interactions to understand the experimentally observed results regarding the tautomeric equilibrium.

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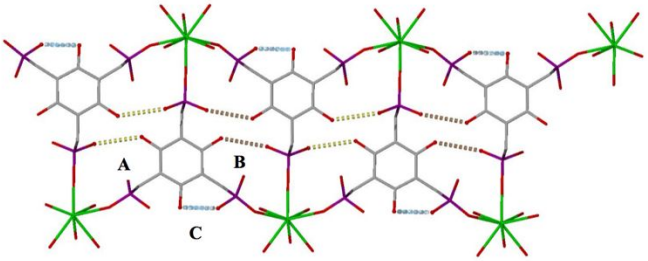

We report synthesis of a new water soluble 1,3,5-trihydroxy-2,4,6-trimethylsulfonic acid benzene and its lanthanide complexes showing the intermolecular H-bonding of 2 OH groups and 2 –OSO2 groups of the adjacent molecules (A and B) and the intramolecular hydrogen bonding of –OH group and –OSO2 groups (C).