

# Iron(II) and sulfate binding by the binucleating ligands O-BISDIEN, O-BISTREN and O-BISBAMP

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## Abstract

One cryptand and two macrocyclic ligands were studied by aqueous potentiometry in the presence and absence of various combinations of ferrous ion and sulfate ions. Appropriate stability constants were computed involving the ligands, hydrogen ion, ferrous ion and sulfate anion. This study is part of an ongoing investigation of binucleating ligands, and is the first report of sulfate binding to ferrous binuclear complexes.

## Introduction

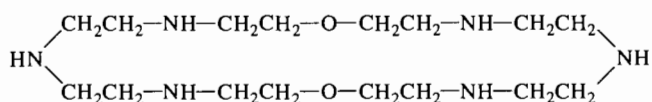
As the result of a review of the literature [1] for common ligands such as ethylenediamine, diethylenetriamine, tetraethylenepentamine, glycine, alanine, nitrilotriacetic acid (NTA), hydroxyethylethylenediaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA), and diethylenetriaminepentaacetic acid (DTPA), a generalization can be formulated that the complexes of  $\text{Fe}^{2+}$  are generally weaker than similar  $\text{Co}^{2+}$  complexes by about 1 log unit for each coordinating amino nitrogen present in the ligand. For polycarboxylic acids such as citric acid, tartaric acid, and oxalic acids no analogous correlation can be made with the number of coordinating carboxylate groups present.

There do not appear to be  $\text{Fe}^{2+}$  binding studies with polyaza macrocycles; however there are several studies reported with aza-thia macrocycles and several derivatized aza-oxa macrocycles [2]. The stability constants of mononuclear metal complexes of these cyclic ligands in each case are less for  $\text{Fe}^{2+}$  than for  $\text{Co}^{2+}$  by up to 3 log units for the  $\text{N}_3$  compounds. Even from this small number of studies there is enough information to demonstrate a sizable macrocyclic effect favoring the binding of  $\text{Fe}^{2+}$  in ring systems over those of analogous open ligand systems. For example, linear DTPA possesses three aliphatic nitrogen donors connected by ethylene bridges with five acetate donor groups. On the other hand, the cyclic [12]ane $\text{N}_3\text{O}_1$ triacetate ligand possesses only three acetate groups, yet the log stability constant with  $\text{Fe}^{2+}$  increases from 16.44 to 16.55 on going from the linear pentaacetate to the cyclic tri-

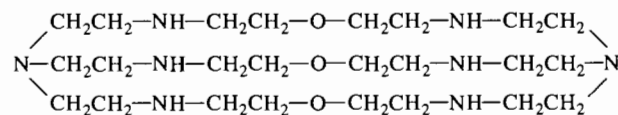
acetate. For reference, the log stability constant of  $\text{Fe}^{2+}$  with EDTA is only 14.3 [3].

There are no examples of iron(II) complexes of polyaza macrocycles in the literature. Likewise there are no examples of studies of any kind of macrocycles with binuclear  $\text{Fe}^{2+}$  complexes although such studies abound for Cu(II) and other metal ions with macrocyclic ligands.

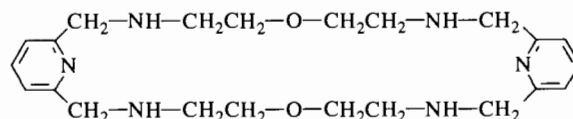
The purpose of this work is to study the mononuclear and binuclear complexes which form between Fe(II) and three macrocyclic and macrobicyclic ligands designed for binucleation and to assess the relative bridging strengths in any sulfate and hydroxo complexes which may be formed. These three ligands are O-BISDIEN, O-BISTREN and O-BISBAMP:



1. O-BISDIEN.



2 O-BISTREN.



3 O-BISBAMP

Sulfate binding is of particular interest because sulfate ion is a necessary constituent when  $\text{Fe}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$  is

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employed. This compound is the most common reagent grade ferrous salt used in investigations of systems with constituents that are usually assumed to be inert to sulfate. Gelb *et al.* [4] have determined the sulfate binding constant for the  $H_4L^{4+}$  form of [18]aneN<sub>6</sub> as 4.18 log units. In addition many other lesser protonated species were found with this binary complex. Dietrich *et al.* [5] studied sulfate binding with the  $H_6L^{6+}$  form of [24]aneN<sub>6</sub> and found 4.05 as the log binding constant while later  $H_5L^{5+}$  and  $H_4L^{4+}$  reactions with sulfate were also detected [6]. Dietrich *et al.* [5] also found the sulfate binding constant with the  $H_6L^{6+}$  form of [27]aneN<sub>6</sub>O<sub>3</sub> to be 4.5 log units and the sulfate binding constant with the  $H_8L^{8+}$  form of [32]aneN<sub>8</sub> to be 4.0 log units, showing that when the charges become widely separated the stability constant starts dropping off. Lehn and co-workers [6, 7] studied two cryptands, O-BIS-TREN and a C<sub>3</sub>-BISTREN trimethylene analog. The hexaprotonated O-BISTREN was found to bind sulfate moderately at 4.90 log units while the analog capable of  $H_8L^{8+}$  protonation possesses the largest binding constant measured yet, 7.45 log units. The hexaprotonated ligand constant is 4.20 log units.

## Experimental

All stability constants were determined by glass and calomel electrode potentiometry using procedures outlined in detail in the literature [8]. The pH set-up was standardized before each titration and the readings were calibrated in terms of p[H] ( $= -\log[H^+]$ ). The experimental conditions were 25.0 °C, with the ionic strength maintained at 0.100 M with KCl. The solutions were generally ~2 millimolar with respect to the ligand and equal to or twice that in the metal ion. Results from both FeSO<sub>4</sub>·7H<sub>2</sub>O (Fisher) and fresh, crystalline Fe(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (Aldrich) were contrasted in this work. The weighed quantity of iron(II) salt was introduced only after at least 4 h into the pre-purged (argon stream cleaned with alkaline pyrogallol) titration cell assembly containing the balance of necessary ingredients by tipping a small boat containing the ferrous salt. Potassium sulfate was obtained from Baker, and KOH Dilutit (Baker) ampoules were used to make up standard 0.1 M KOH solution. Other reagents were of reagent grade quality. Doubly distilled water (KMnO<sub>4</sub>) was used throughout. The ligands O-BISDIEN and O-BISTREN were obtained as hexahydrobromide salts kindly donated by Dr Ichiro Murase of Dojindo & Company, Kumamoto, Japan. The O-BISBAMP was resynthesized specifically for this work by the previously published method [9].

The following generalized potentiometric titration paradigm was followed with each of the three ligands studied:

No. 1. Ligand alone

No. 2. Ligand and K<sub>2</sub>SO<sub>4</sub> 1:1

No. 3. Ligand, Fe(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O 1:1

No. 4. Ligand, Fe(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O 1:2

No. 5. Ligand, FeSO<sub>4</sub>·7H<sub>2</sub>O 1:1

No. 6. Ligand, FeSO<sub>4</sub>·7H<sub>2</sub>O 1:2

Each potentiometric titration was done singly unless problems became apparent. There were usually some 70 to 100 points obtained per p[H] profile providing in general at least 10 pairs of data (volume base, p[H]) per neutralization equivalent. All ferrous titrations were essentially colorless until the cell was opened after the conclusion of the determination, when suddenly iron(III) hydroxide precipitated because of rapid oxidation. Computations were all carried out with the program BEST [8] and species visualizations were realized with SPE [8] and rendered on the Laser Jet II using SPEPLOT [8].

## Results

### Protonation constants

The protonation constants obtained in this work, listed in Table 1, are in excellent agreement with previously published work. The minor differences can be accounted for in terms of usually expected uncertainties inherent in using different salts, different samples and work done by different researchers. The higher protonation constants  $K_{4-6}$  in O-BISTREN, over those in the previous work, reflect residual chloride binding, a factor which is constant in this work. Binding of Cl<sup>-</sup> is in effect taken care of by the supporting electrolyte and is not part of this investigation.

It was imperative to remeasure the protonation constants under the exact conditions of this work in order to minimize such variations as are apparent from the comparisons in Table 1 with the previously measured protonation constants of these three ligands. The current protonation constants are the basis of the following ferrous binding and sulfate binding experiments. The internal consistency is evidenced by the overall  $\sigma_{fit} = 0.003$  in each case.

### Ligand sulfate binding

Analysis of pH profiles for O-BISDIEN in the absence and presence of sulfate shows that three well-defined sulfate species are formed with this ligand:



TABLE 1. Protonation constants at 25.0 °C in 0.100 M KCl

|                       | O-BISDIEN |                    | O-BISBAMP |                    | O-BISTREN |                          |
|-----------------------|-----------|--------------------|-----------|--------------------|-----------|--------------------------|
|                       |           | (Lit) <sup>a</sup> |           | (Lit) <sup>b</sup> |           | (Lit) <sup>c, d, e</sup> |
| Log $K_1$             | 9.62      | (9.65)             | 8.83      | (8.75)             | 9.88      | (9.89)                   |
| Log $K_2$             | 8.88      | (8.92)             | 7.97      | (7.94)             | 9.20      | (9.23)                   |
| Log $K_3$             | 8.28      | (8.30)             | 7.36      | (7.36)             | 8.29      | (8.29)                   |
| Log $K_4$             | 7.62      | (7.64)             | 6.81      | (6.79)             | 7.84      | (7.65)                   |
| Log $K_5$             | 3.81      | (3.81)             |           |                    | 7.29      | (6.64)                   |
| Log $K_6$             | 3.30      | (3.26)             |           |                    | 6.55      | (6.01)                   |
| $\sigma_{\text{fit}}$ | 0.003     |                    | 0.003     |                    | 0.003     |                          |

<sup>a</sup>Ref. 1. <sup>b</sup>Ref. 9. <sup>c</sup>Ref. 10. <sup>d</sup>Ref. 11. <sup>e</sup>In 0.100 M NaClO<sub>4</sub> medium, 25.0 °C

These findings indicate that below p[H] 7 the predominant forms of the free ligand are sulfate containing forms when the sulfate ion is equimolar (or larger) with respect to the ligand concentration. The relative stabilities of these complexes are clearly indicated by the species distribution curves in Fig. 1.

The sulfate interactions with O-BISTREN are interesting since five species were found:



The only major species through p[H] 6.5 is  $\text{H}_6\text{LSO}_4^{4+}$  partly because its equilibrium constant is largest and partly because there are no other competing equilibria.

The pyridine-containing ligand O-BISBAMP can protonate only four times. The following four equations



were used to describe the sulfate containing system and hence derive the associated stability constants. The second and fourth sulfato complexes,  $\text{H}_3\text{LSO}_4^{1+}$  and  $\text{HLSO}_4^{1-}$  are very minor species indeed. The species  $\text{H}_3\text{LSO}_4^{1+}$  is minor because the species  $\text{H}_4\text{LSO}_4^{2+}$  appears to be unusually stable in that it persists well into the p[H] region where  $\text{H}_3\text{L}^{3+}$  is fully formed. Further deprotonation of the ligand depletes the concentrations of the other protonated sulfato species. These minor sulfato species were found since a larger than 1:1 sulfate to ligand ratio was employed in this potentiometric titration. The relative stabilities and relative concentrations of these sulfato complexes of the protonated forms of the ligand are indicated by the species distribution curves in Fig. 2.

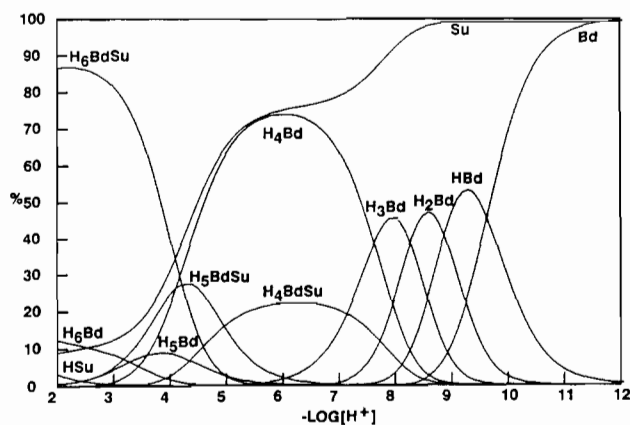


Fig. 1. Distribution of species as a function of p[H] for the system containing 0.0192 M sulfate and 0.00194 M O-BISDIEN at 25.0 °C and 0.100 M ionic strength (KCl). Su =  $\text{SO}_4^{2-}$  and Bd = O-BISDIEN, % = percent of complex formed relative to total concentrations of O-BISDIEN or  $\text{SO}_4^{2-}$  present.

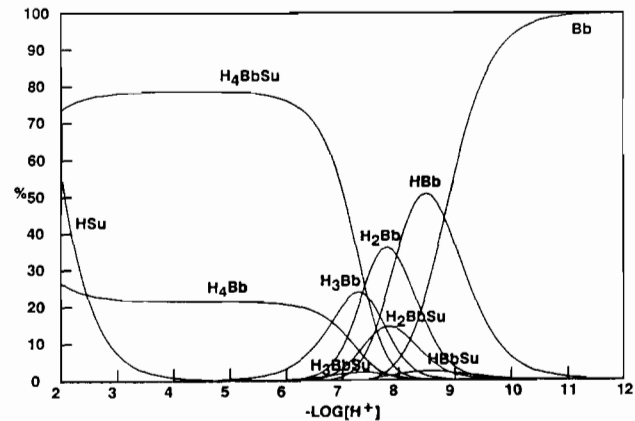
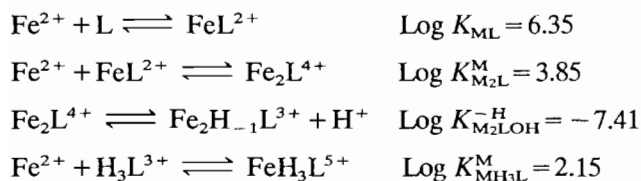


Fig. 2. Distribution of species as a function of p[H] for the system containing 0.00223 M O-BISBAMP and 0.00653 M  $\text{SO}_4^{2-}$  at 25.0 °C and 0.100 M ionic strength (KCl). Su =  $\text{SO}_4^{2-}$  and Bb = O-BISBAMP, % = percent of complex formed relative to total concentrations of O-BISBAMP species set at 100%.

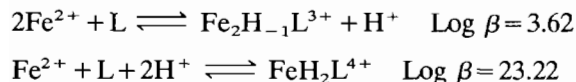
### Ferrous binding

According to items No. 3 and No. 4 of the titration paradigm, potentiometric p[H] data for the ferrous-ligand systems were employed to calculate 1:1 and 2:1 metal:ligand binding constants of 1:1 and 2:1 complexes, together with constants involving protonated and deprotonated species. The results obtained for O-BISDIEN in the absence of sulfate (using ferrous perchlorate) are:

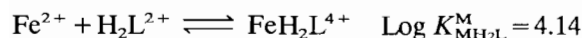


The absence of  $\text{FeH}_2\text{L}^{4+}$  and  $\text{FeHL}^{3+}$  species is understood by examination of the species distribution diagram of the system containing a 2:1 molar ratio of Fe(II) to O-BISDIEN (Fig. 3). The species  $\text{FeH}_3\text{L}^{5+}$  is only an intermediate toward the formation of dinuclear species  $\text{Fe}_2\text{L}^{4+}$  and its very stable hydroxo-bridged  $\text{Fe}_2\text{H}_{-1}\text{L}^{3+}$  form. In fact above p[H] the system is dominated by the hydroxo-bridged dimer with only a minor amount of the mononuclear complex in equilibrium with it.

Calculation of the 1:1 and 2:1 ferrous:O-BISTREN systems showed that only two ferrous-containing species are needed to accurately describe both potentiometric titration curves. Because stepwise formation constants could not be obtained, only overall log  $\beta$ s were therefore computed:



or



The inability to calculate stepwise formation constants is due to the high stability of the hydroxo-bridged dinuclear iron(II) complex resulting in making the concentration of the binuclear complexes  $\text{Fe}_2\text{L}^{4+}$  so small as to be undetectable by potentiometric measurements. Thus neither the constant for its formation from the mononuclear complex nor its hydrolysis constant to the hydro-bridged species could be determined. These two species are important in both 1:1 and 2:1 solutions with  $\text{Fe}_2\text{H}_{-1}\text{L}^{3+}$  complex predominating above p[H] 8, as seen in the species distribution curves of Fig. 4 for the 2:1 ferrous-O-BISTREN system solution. The hydroxo-bridged dinuclear complex is so stable that it also predominates in the 1:1 system (not shown). The results show the strong tendency for self-assembly of the hydroxo-bridged dinuclear iron(II) complex.

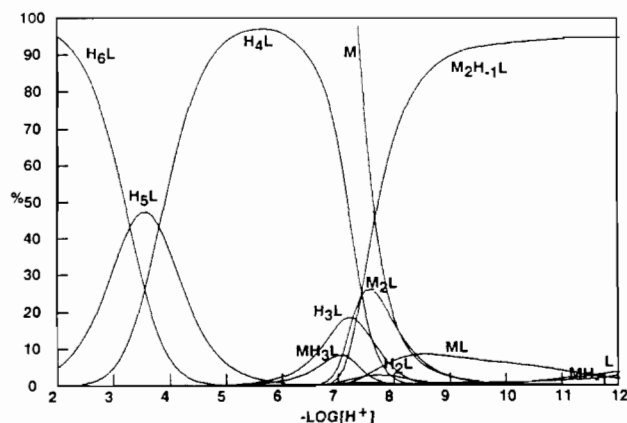


Fig. 3. Distribution of species as a function of p[H] for the system containing 0.00208 M O-BISDIEN and 0.00403 M Fe(II) at 25.0 °C and 0.100 M ionic strength (KCl) L=O-BISDIEN and M=Fe<sup>2+</sup>, %=percent of complex formed relative to total concentrations of O-BISDIEN species set at 100%.

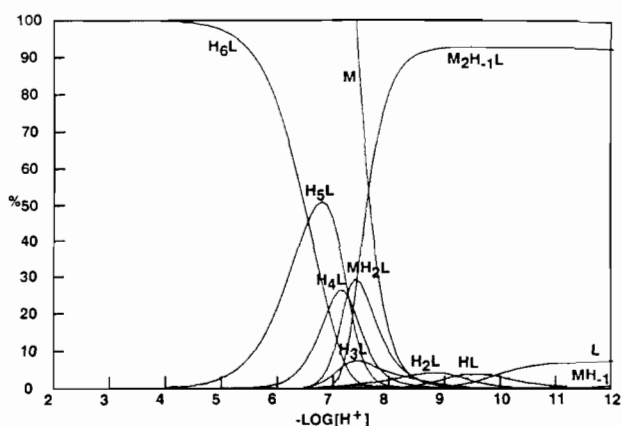
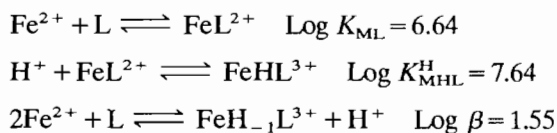


Fig. 4. Distribution of species as a function of p[H] for the system containing 0.00212 M O-BISTREN and 0.00393 M Fe(II) at 25.0 °C and 0.100 M ionic strength (KCl) L=O-BISTREN and M=Fe<sup>2+</sup>, %=percent of complex formed relative to total concentrations of O-BISTREN species set at 100%.

O-BISBAMP behaves differently in that a 1:1 formation constant could be calculated. In addition a 1:1 monoprotonated complex and a dinuclear hydroxo-bridged complex were found:



All of the species are significant and the complexes formed are major components of the 1:1 and 2:1 systems. However, it is important to note the fact that there is

much less tendency for  $\text{Fe}_2\text{H}_{-1}\text{L}^{3+}$  to form in 1:1 solutions. This is due to the fact that its formation constant is considerably lower (it is lower than that of O-BISTREN by about two orders of magnitude, as seen from the  $\beta$  values). This in turn made possible the calculation of the two 1:1 species.

#### Ligand-ferrous sulfate binding

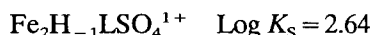
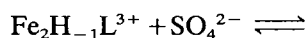
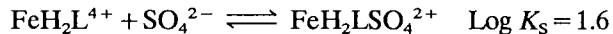
Comparison of the pH profiles obtained for the Fe(II) complexes with and without sulfate was used to determine specific sulfate-metal-ligand binding constants.

When O-BISDIEN is studied by potentiometric pH measurements in the presence of equimolar sulfate anion (Bd:Fe:SO<sub>4</sub> = 1:1:1 and 1:2:2) the computer computations reject any model except that involving one new  $\text{FeH}_3\text{LSO}_4^{3+}$  species:



This species is formed to a maximum amount around p[H] 7, as seen in the species distribution curve (Fig. 5). But the tendency toward hydroxo-bridged dinuclear complex is so great that this structure soon disappears above p[H] 7.5. At lower p[H] the sulfate anion is bound by the protonated forms of the metal-free ligand.

O-BISTREN also promotes the formation of a mononuclear complex but with the involvement of one less proton. Of special interest is the discovery of the formation of a dinuclear dibridged cryptate:



The formation constants are not large, but Fig. 6 shows that a substantial fraction of the solution above p[H] 7.5 is the sulfato and hydroxo-bridged complex.

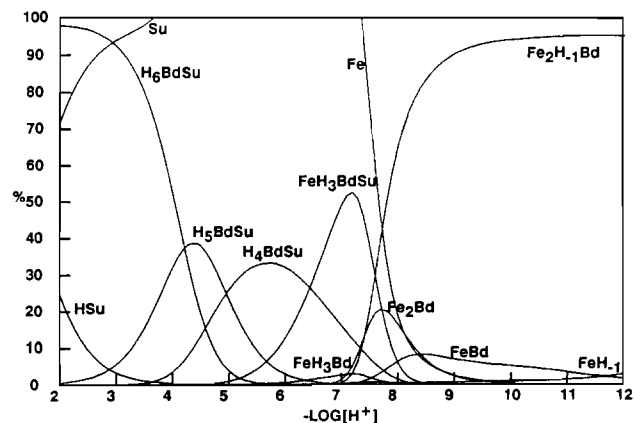


Fig. 5. Distribution of species as a function of p[H] for the system containing 0.00205 M O-BISDIEN and 0.00400 M SO<sub>4</sub><sup>2-</sup> at 25.0 °C and 0.100 M ionic strength (KCl). % = percent of complex formed relative to total concentrations of O-BISDIEN species set at 100%. Free O-BISDIEN species are not shown.

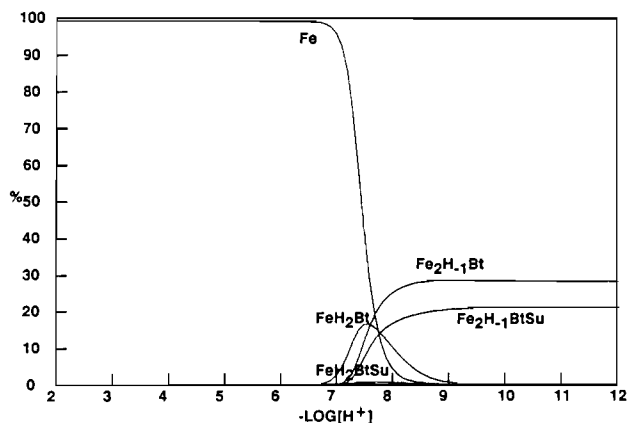


Fig. 6. Distribution of Fe(II)-containing species as a function of p[H] for the system containing 0.00215 M O-BISTREN and 0.00213 M SO<sub>4</sub><sup>2-</sup> at 25.0 °C and 0.100 M ionic strength (KCl). Bt = O-BISTREN, Fe = Fe<sup>2+</sup>, and Su = SO<sub>4</sub><sup>2-</sup>. % = percent of complex formed relative to total concentrations of O-BISTREN species set at 100%.

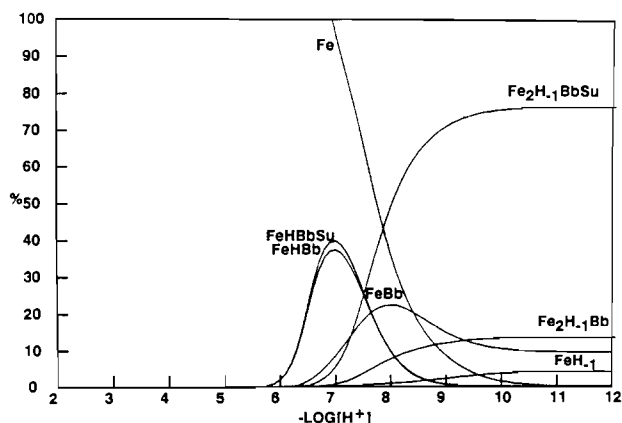
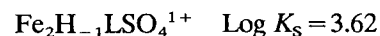
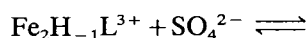


Fig. 7. Distribution of Fe(II)-containing species as a function of p[H] for the system containing 0.00116 M O-BISBAMP, 0.00226 M Fe(II), and 0.00226 M SO<sub>4</sub><sup>2-</sup> at 25.0 °C and 0.100 M ionic strength (KCl). Bb = O-BISBAMP, Fe = Fe<sup>2+</sup>, and Su = SO<sub>4</sub><sup>2-</sup>. % = percent of complex formed relative to total concentrations of O-BISBAMP species set at 100%.

Finally, sulfate binding to O-BISBAMP has been measured. A strong MHL sulfato complex was found, together with a binuclear dibridged dimer containing a sulfate anion:

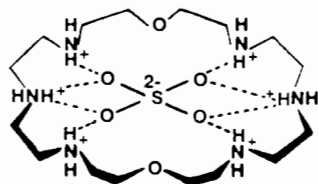


The species curves in Fig. 7 show the formation of the mononuclear monoprotonated sulfato complex with a maximum concentration at p[H] 7, but with the dibridged dinuclear species predominating in alkaline solution.

## Discussion

### Sulfate binding by the protonated ligands

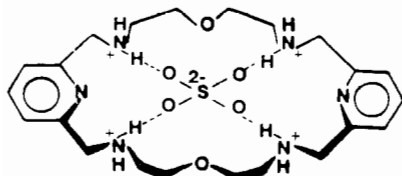
Sulfate binding by hexaprotonated O-BISDIEN is characterized by the highest binding constant  $K_S^6$  of all the ligand species in this investigation, and is larger by one half log unit than that reported for any  $N_6$  macrocycle studied previously. The sulfate ion is considered bound both by hydrogen bonds and by coulombic forces. Formula 4 gives an example of the possible hydrogen bonding modes between the sulfate ion and the protonated amino groups of the ligand. It is important to observe that 4 is not a representation of the structure of the sulfato-protonated ligand complex.



4: Sulfate complex of hexaprotonated O-BISDIEN,  $H_6LSO_4^{4+}$ .

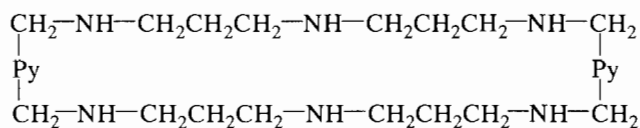
The magnitudes of the  $\log K_S$  values for sulfate binding to protonated O-BISTREN are found to be smaller than expected based on the report of Lehn and co-workers [7] ( $\log K_S^6 = 4.90$ ;  $\log K_S^5 = 2.90$ ) and more sulfato-bound species were discovered in this work. The formation of species  $H_5LSO_4^{3+} - H_2LSO_4^{0+}$  are very overlapping and minor, as are the major non-sulfato-bound protonated ligand species  $H_5L^{5+} - H_2L^{2+}$ . The background electrolyte in the previous work was sodium tosylate under the concept that the tosylate anion would not fit into the crypt.

The most stable of the O-BISBAMP sulfato complexes,  $H_4LSO_4^{2+}$ , has the maximum number of hydrogen bonds, involving four protons, between the hexaprotonated ligand and the sulfate anion. The hydrogen bonding modes, indicated by formula 5, is visualized as involving a hydrogen bond between each of the protonated aliphatic amino groups of the ligand and each of the sulfate oxygens. The stability of this complex is due not only to the hydrogen bonds, but to coulombic forces and the symmetry of the complex.



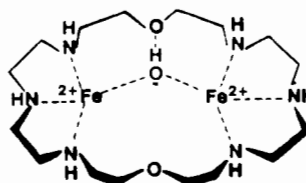
5: Sulfate complex of tetraprotonated O-BISBAMP,  $H_4LSO_4^{2+}$ .

Wu *et al.* [12] studied the only other pyridine-containing macrocycle,

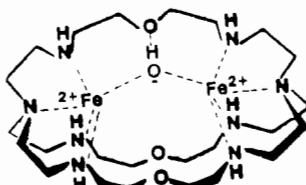


and found  $\log K_S^4 = 2.79$ . This ligand is not completely analogous since it has  $-NH-$  bridges in place of ether oxygens, but is isoelectronic with the O-BISBAMP ligand. It may be fortuitous that they obtained a very similar value for the sulfato binding constant. Unfortunately, the literature yields no other examples for comparison.

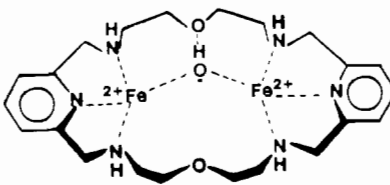
The Fe(II)-ligand systems in the presence and absence of sulfate ions are dominated by the formation of the relatively very stable  $\mu$ -hydroxo binuclear Fe(II) complexes. This species is so stable that it predominates even in 1:1 systems which are designed to favor mononuclear complexes. Visualization of the coordinate bonding modes in the hydroxo-bridged binuclear iron(II) complexes of the three ligands is indicated by formulas 6-8. In all cases the hydroxide ion is indicated as bridging because it is formed at a lower  $p[H]$  than is the hydroxo complex of the Fe(II) ion. These complexes are analogous to the binuclear hydroxo-bridged copper O-BISTREN complex, which has been described in considerable detail [13].



6: Hydroxo-bridged binuclear Fe(II) O-BISDIEN complex,  $Fe_2H_{-1}L^{3+}$ .

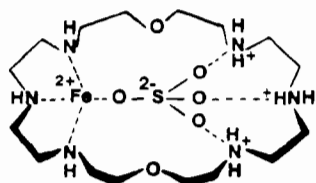


7: Hydroxo-bridged binuclear Fe(II) O-BISTREN complex,  $Fe_2H_{-1}L^{3+}$ .

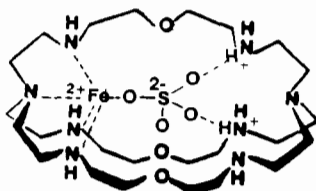


8: Hydroxo-bridged binuclear Fe(II) O-BISBAMP complex,  $Fe_2H_{-1}L^{3+}$ .

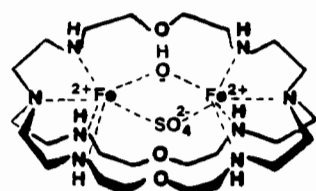
The sulfato adducts of these macrocyclic complexes are bound by coordinate bonds, and in some cases by both coordinate bonds and hydrogen bonds. The mononuclear complexes of O-BISDIEN and O-BISTREN,



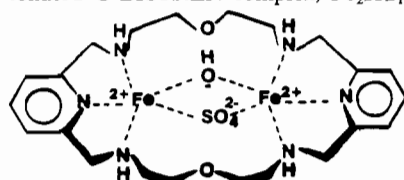
9: Sulfate adduct of mononuclear Fe(II) triprotonated O-BIS-DIEN complex,  $\text{FeH}_3\text{LSO}_4^{3+}$ .



10: Sulfate adduct of mononuclear Fe(II) diprotonated O-BIS-TREN complex,  $\text{FeH}_2\text{LSO}_4^{2+}$ .



11: Sulfate adduct of hydroxo-bridged binuclear Fe(II) deprotonated O-BISTREN complex,  $\text{Fe}_2\text{H}_{-1}\text{LSO}_4^+$ .



12: Sulfate adduct of hydroxo-bridged binuclear Fe(II) O-BISBAMP complex,  $\text{FeH}_{-1}\text{LSO}_4^+$ .

formulas **9** and **10**, bind sulfate through coordination to the iron(II) and by hydrogen bonding to the positive protonated amino nitrogens of the ligand. In the binuclear complexes of O-BISTREN and O-BISBAMP,

the sulfato group is believed to bridge and coordinate the two metal ions in the manner suggested by formulas **11** and **12**.

### Acknowledgements

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