consistent with the data in Table V. Although the relative constancy of k_{1p} does not establish the pathway as being FeOH + HL for all these systems, this fact, plus the other observations, argues for the assignment of the rate constants to k_5 as indicated in Table V. If k_{1p} is on the order of 10^1 sec^{-1} for the k_1 pathway, then the contributions from this pathway to the measured rate would be quite small for ligands which are mostly protonated in acid solutions.

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Registry No. Fe^{3+}, 20074-52-6; C_6H_5OH, 108-95-2; *o*-$H_2NC_6H_4OH$, 95-55-6.

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Iron(III) Chelate Complexes of Hydrogen Sulfide and Mercaptans in Aqueous Solution

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Iron(III) *N*-hydroxyethylethylenediaminetriacetate (Fe^{III}HEDTA) and other iron(III) chelates react with hydrogen sulfide and mercaptans in aqueous solution. Unstable pink complexes form. Fe^{III}HEDTA forms a complex with 2 mol of iron chelate per mole of H_2S ($K = 4.4 \times 10^6$; λ_{max} 490 nm; ϵ_{max} 8900). With other mercaptans (mercaptoethanol, ethyl mercaptan, L-cysteine), 1:1 complexes are formed ($K = 10$; λ_{max} 530 nm; ϵ_{max} 3200). The stoichiometry of the complex is assigned on the basis of an iterative procedure applied to spectrophotometric data determined for maximum extent of complex formation. Esr spectra of these complexes show a sharp peak superimposed upon a broad peak at $g = 4.3$.

Introduction

The structure and the hydrolytic properties of the iron(III) chelate of *N*-hydroxyethylethylenediaminetriacetic (HEDTA) have been extensively studied.[2-6] In view of the preceding work on the aqueous iron(III) chelate systems, it seemed reasonable to assume that these complexes contained a *hard core primary coordination polyhedron* at iron with at least one available uncoordinated or weakly coordinated position which could readily accommodate a good nucleophilic ligand. We were interested in the reactions of these iron chelates with hydrogen sulfide and mercaptans in aqueous solution.

Experimental Section

Chemicals. Chemicals were obtained from the following sources: potassium chloride, ferric sulfate, and ferrous sulfate from Fisher Scientific Co.; HEDTA from Eastman Co.; $Na_2EDTA \cdot 2H_2O$ from J. T. Baker Chemical Co.; hydrogen sulfide from Matheson Co.; 2-mercaptoethanol and ethyl mercaptan from Pfaltz and Bauer, Inc.; L-cysteine hydrochloride, mercaptoacetic acid, and methyl mercaptan (gaseous) from Aldrich Chemical Co. All chemicals were used without further purification.

Solutions. All solutions were made in deionized distilled water which had been deoxygenated by bubbling with nitrogen. Once prepared, solutions were again bubbled with nitrogen and stored under a nitrogen atmosphere. Ferric HEDTA solution was made from standardized ferric sulfate and standardized HEDTA solutions. The pH of chelate solutions was adjusted by adding 2.0 *M* NaOH. In order to maintain constant ionic strength during each study, 0.4 mol of KCl was added per liter of the solution. Also, a 2% excess of HEDTA was maintained in the ferric HEDTA solutions. Similarly, ferric EDTA solutions were made by mixing standardized solutions of ferric sulfate and EDTA, etc.

Saturated solutions of ethyl mercaptan were made in cold water. Gaseous methyl mercaptan was dissolved in ice-cold water. L-Cysteine hydrochloride (99%) was dissolved in water and sufficient NaOH was added to raise the pH to 7. Dilutions to required strength were made from this stock solution.

Hydrogen sulfide wad dissolved in cold nitrogen-saturated water and diluted to required concentration. All mercaptan and hydrogen sulfide solutions were standardized by titration with standardized silver nitrate solution using silver electrode potentiometric end point detection.

Flow System. Since the complexes formed between iron(III) chelates and sulfur ligands are inherently unstable, all the spectrophotometric studies were carried out using a specially devised flow system consisting of two cylindrical reservoirs of identical diameter, each with a capacity of 2 l. and a height of about 20 in. A constant pressure of 14 psi could be maintained by connecting the upper reservoir inlets to a nitrogen supply. Two liters each of standardized solutions of iron(III) chelate and mercaptan were stored in separate wash bottles. The solutions were transferred into the reservoirs *via* lower reservoir inlets by nitrogen pressure. The separate solutions of iron(III) chelate and mercaptan or hydrogen sulfide were mixed using a four-jet mixing chamber (Varian Associates) and allowed to flow through a quartz spectrophotometer cell of 5.0-mm path length. The visible spectra of the resulting solutions were scanned at various flow rates using a Cary 14 spectrophotometer. The dead time (time for flow between mixer and cell) was 0.1 sec at 5 ml/sec flow rates. Spectra were obtained at 25 ± 1° in the presence of 0.2 *M* KCl. Other salts (KNO_3, K_2SO_4) proved equally effective at maintaining ionic strength.

The effluent from the flow cell was passed through a small cell containing a glass electrode and KCl bridge to a standard calomel electrode allowing pH determination.

For every pair of iron(III) chelate and mercaptan (or H_2S) concentrations, the stopped-flow spectrophotometric recordings were repeated ensuring reproducibility. When absorbance was measured at constant wavelength (490 or 530 nm), absorption maximum was reached shortly after the flow was stopped and decay of the absorbance with time was easily measured.

Esr Studies. Esr experiments were performed using a Varian E-6S spectrometer. An esr flow system was used for mixing the solution.[7] One end of an open ended quartz tube was attached to

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the outlet of the four-jet mixing chamber. The mixture was allowed to flow through the tube. The flow was stopped by closing the other end of the quartz tube with a specially fabricated plastic plug. The tube was detached from the mixer outlet and immediately but carefully frozen in liquid nitrogen. No more than 10 sec was required for complete freezing of the sample after mixing. Samples were prepared at different time intervals by extending the time interval between stopping the flow through the quartz tube and freezing. The total initial concentration of $Fe^{III}HEDTA$ was maintained at 10^{-2} *M* for all esr studies. A large excess of mercapto compound was used to maintain the highest concentration levels possible of iron-sulfur complex.

Results and Discussion

When solutions of $Fe^{III}HEDTA$ at pH 6.5 and hydrogen sulfide are mixed in the flow system, the formation of an intensely colored soluble complex is initiated. The rate of flow of the mixture through the flow cell controls the concentration of the colored complex in the light path of the spectrophotometer. At a flow rate of 1 ml/sec the absorption spectrum of the complex is scanned in the visible region. The visible spectrum of the complex reveals an absorption maximum at 490 nm. At fast flow rates (5 ml/sec or more) the peak height at 490 nm is considerably smaller. Sudden stopping of a fast flow allows the maximum formation of the complex in the spectrophotometric cell as it is indicated by a sharp increase in the intensity of absorption at 490 nm. When the fast flow is stopped, the maximum peak height attained at 490 nm is almost entirely due to the absorption of the iron-sulfur complex and the dimeric species of $Fe^{III}HEDTA$ system. The molar extinction coefficient of the latter species is appreciably smaller than that of the complex. The exact contribution to the peak height at 490 nm by the dimeric species of $Fe^{III}HEDTA$ can be calculated. Parallel observations were made when mercapto compounds replaced hydrogen sulfide. Most iron chelate-mercaptan complexes studied have absorption maxima near 530 nm.

Stoichiometry. An iteration procedure was developed which assumed a fixed stoichiometry for complex formation and calculated stability constants from raw data assuming that stoichiometry. Incrementally increased values of the molar extinction coefficient were assigned to the complex. A stoichiometry was assigned when the average relative per cent deviation reached a minimum and when no concentration-dependent trends in values of computed equilibrium constants were apparent. The molar extinction coefficient was assigned on the basis of minimum average relative per cent deviation. The general reaction between iron(III) chelate and mercaptan can be formulated using $Fe^{III}HEDTA$ as an example

$$\begin{array}{l} 2Fe^{III}HEDTA\cdot OH^- \rightleftharpoons [Fe^{III}HEDTA]_2O^{2-} + H_2O \\ \quad 2RSH \downarrow \uparrow \\ 2Fe^{III}HEDTA\cdot SR^- + 2H_2O \end{array} \qquad (1)$$

$$K = \frac{[Fe^{III}HEDTA\cdot SR^-]}{[Fe^{III}HEDTA\cdot OH^-][RSH]} \qquad (2)$$

$$= \frac{[\text{monomeric mercaptide}]}{[\text{monomeric hydroxide}][RSH]}$$

The hydrogen sulfide reaction is best accounted for by the equations

$$\begin{array}{l} 2Fe^{III}HEDTA\cdot OH^- \rightleftharpoons [Fe^{III}HEDTA]_2O^{2-} + H_2O \\ \quad H_2S \downarrow \uparrow \\ [Fe^{III}HEDTA]_2S^{2-} + 2H_2O \end{array} \qquad (3)$$

The data obtained by the iterative procedures are summarized in Table I.

Ethyl mercaptan reacts with $Fe^{III}HEDTA$ at pH 6.5 to form a complex which has a visible absorption very similar to those of other mercaptide complexes. However, the ethyl mercaptide complex decomposes steadily, and the formation of a second complex is observed. The rate of formation and the final concentration of the second complex is dependent on the initial concentrations of $Fe^{III}HEDTA$ and ethyl mercaptan solutions. The higher the concentration of either reactant, the faster is the rate of formation and higher the concentration of the second complex formed. Very low concentrations of either reactant cannot initiate the formation of the second complex, even when the formation and decomposition of the first complex is spectrophotometrically observed. The nature of the second complex has not been determined. The second complex has a slightly longer wavelength absorption maximum in the visible region (540 nm) as compared to the absorption maximum of the first complex. The spectrum was scanned in the visible region after the formation of the second complex reached the maximum concentration as indicated by the intensity of absorption at 530 nm. The second complex is more stable than any other sulfur complex we have investigated. Methyl mercaptan is not very soluble in water, and the estimation of its concentration is quite difficult. The complex formed between Fe^{III}-HEDTA and methyl mercaptan at pH 6.5 decomposes much faster than other thiol complexes. We were unable to obtain any spectral evidence indicating the formation of a second complex as the first methyl mercaptan complex decomposed.

In the case of the $Fe^{III}EDTA$-cysteine system, the *hard core* primary chelation at iron(III) is slightly changed. The model complex formed by $Fe^{III}EDTA$ at pH 7.6 and cysteine at pH 7.0 is very similar to the $Fe^{III}HEDTA$-cysteine complex. Since the complexes formed by iron(III) chelates and mercaptans decompose at higher alkaline pH values, the completely hydrolyzed $Fe^{III}EDTA$ formed at a pH above 9 was not used. The $Fe^{III}EDTA$ system at pH 7.6 is composed of several species including hydrated monomer, monohydroxy monomer, and some dimers. We have assumed that Fe^{III}-EDTA is primarily monomeric and calculated the stability constant K as in eq 4.

$$K = \frac{[Fe^{III}EDTA\cdot SCy]}{([\text{total } Fe^{III}] - [Fe^{III}EDTA\cdot SCy])[CySH]} \qquad (4)$$

Esr Studies. At room temperature, neither $Fe^{III}HEDTA$ nor the mercaptide complexes show any esr signals. Studies were carried out at 77°K. A frozen sample of $Fe^{III}HEDTA$ has a broad signal at $g = 4.3$.

The esr spectra of the frozen samples of model complexes formed between $Fe^{III}HEDTA$ and mercaptans or hydrogen sulfide have a sharp signal superimposed on a broad signal around $g = 4.3$. The relative intensity of the sharp signal increases with the increase in the concentration of mercaptan present in the system. When the complex is allowed to decompose for some time before the samples are frozen, the esr spectrum of the system indicates that the intensity of both the sharp and the broad signals centered around $g = 4.3$ decreases in proportion to the time of decomposition. When the samples are allowed to decompose completely, their spectra do not show either a sharp signal or a broad signal at $g = 4.3$. The broad signal at $g = 4.3$ is assigned to iron(III) chelated by HEDTA. The sharp signal at $g = 4.3$, which is superimposed on the broad signal, is assigned to the high-

Table I. Summary of Stability Constants and Stoichiometry of Model Complexes[a]

Iron(III) chelate[b]	Sulfhydryl compd[b]	Formulation of complex	Molar extinction coeff at min % dev of K	K
$Fe^{III}HEDTA$	H_2S	$[Fe^{III}HEDTA]_2S^{2-}$	8900 (490 nm)	4.4×10^6
$Fe^{III}HEDTA$	Mercaptoethanol	$Fe^{III}HEDTA \cdot SR^-$	3100 (530 nm)	6.0
$Fe^{III}HEDTA$	L-Cysteine	$Fe^{III}HEDTA \cdot SCy^-$	3320 (530 nm)	15.2
$Fe^{III}EDTA$	L-Cysteine	$Fe^{III}EDTA \cdot SCy^-$	3300 (530 nm)	8.6
$Fe^{III}HEDTA$	Ethyl mercaptan	$Fe^{III}HEDTA \cdot SEt^-$	3200 (530 nm)	3.9

[a] Temperature 25 ± 1°; $\mu = 0.2$ *M*, KCl. [b] Approximate ranges of concentration: H_2S, 10^{-4}-10^{-2} *M*; mercaptoethanol, 10^{-2}-1 *M*; L-cysteine, 10^{-3}-10^{-1} *M*; ethyl mercaptan, 10^{-2}-10^{-1} *M*.

spin iron(III) in the model thiol complex.[8] No signal near $g = 2$ due to an iron-sulfur species was detected upon cooling the $Fe^{III}HEDTA$-H_2S system to 4° K.[9]

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Registry No. $[Fe^{III}HEDTA]_2S^{2-}$, 39459-79-5; $Fe^{III}HEDTA \cdot SCH_2CH_2OH^-$, 39452-75-0; $Fe^{III}HEDTA \cdot SCy^-$, 39452-77-2; $Fe^{III}EDTA \cdot SCy^-$, 39452-76-1; $Fe^{III}HEDTA \cdot SEt^-$, 39452-74-9.

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The Ligand Pentaammine(pyrazine)ruthenium(II). Aqueous Complexes of Nickel(II), Copper(II), and Zinc(II)

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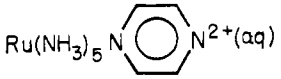
Association quotients for aqueous complexes of the bipositive ligand pentaammine(pyrazine)ruthenium(II) with nickel(II), copper(II), and zinc(II) have been determined by spectrophotometry, using the bathochromic shift of the ruthenium(II)-pyrazine electron-transfer band. For nickel(II) the association quotient is 17 ± 2 M^{-1} while the parameters ΔH and ΔS are −6 ± 0.8 kcal/mol and −15 ± 3 cal deg^{-1} mol^{-1}, respectively, at 25°, $\mu = 1.5$ *M*, and pH 3.9-6. For the copper(II) adduct those quantities are 32 ± 3 M^{-1}, −4.3 ± 0.5 kcal/mol, and −7 ± 2 cal deg^{-1} mol^{-1}, respectively, at 25° and $\mu = 1.0$ *M*. For zinc(II) the association quotient is 3.1 ± 0.5 M^{-1} with ΔH and ΔS equal to −4.3 ± 0.5 kcal/mol and −12 ± 3 cal deg^{-1} mol^{-1} at 25° and $\mu = 2.0$ *M*. The rate constants for formation and dissociation of the nickel(II) complex were also determined, yielding for k_1, $\Delta H^{\ddagger}_1$, and $\Delta S^{\ddagger}_1$ the values (1.1 ± 0.1) × 10^3 M^{-1} sec^{-1}, 10 ± 1 kcal/mol, and −11 ± 3 cal deg^{-1} mol^{-1}, respectively, at 25° and $\mu = 1.0$ *M*. For the reverse reaction k_{-1}, $\Delta H^{\ddagger}_{-1}$, and $\Delta S^{\ddagger}_{-1}$ were found to be 66 ± 5 sec^{-1}, 16 ± 1 kcal/mol, and 4 ± 3 cal deg^{-1} mol^{-1}, respectively. The results are related to the basicity of the pentaammine(pyrazine)ruthenium(II) complex.

Introduction

An especially interesting property of the aqueous ion pentaammine(pyrazine)ruthenium(II), Ru(pz) (I), is that, when



I

protonated at the free electron pair of pyrazine, the complex has a pK_a value of 2.6.[1,2] In comparison, the pK_a of the free, aqueous pyrazinium ion is only 0.6.[3] On protonation of Ru(pz), the metal-to-ligand ($\pi^* \leftarrow t_{2g}$) electron transfer band of the complex is shifted to lower energy. Both the energy shift and the increased pK_a of pyrazine when coordinated to ruthenium(II) have been attributed to increased metal-to-ligand back-donation in the protonated complex, relative to the unprotonated ion.[2,4]

We have found that Ru(pz) can associate with several aqueous, first-row transition metal ions to form binuclear complexes. The existence of these complexes demonstrates that the basicity of pyrazine in the Ru(pz) moiety is sufficient to balance the repulsion between the two positively

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