Selection of new Fe(III)/Fe(II) chelating agents as catalysts for the oxidation of hydrogen sulfide to sulfur by air

Arthur E. Martell, Ramunas J. Motekaitis, Dian Chen, Robert D. Hancock, and Derek McManus

Abstract: The removal and oxidation to sulfur of H_2S, contained in a broad range of sour gas streams including natural gas, by a Fe(III)/Fe(II) chelate system imposes several requirements on the iron chelate that is employed as the redox catalyst. The solution of the catalyst must be neutral or mildly alkaline to efficiently absorb H_2S from the gas passed through the solution. The stability of the iron(III) chelate must be high enough that solid $Fe(OH)_3$ not precipitate at the pH employed. Also the stability of the iron(II) chelate must be high enough to prevent the precipitation of FeS from the reaction mixture. The difference in stabilities of the Fe(III) and Fe(II) chelates must be low enough so that the Fe(III) form can be reduced by HS^- and that the Fe(III) chelate can be regenerated by aeration of the solution at alkaline pH. An unexpected result of this study is that chelating agents designed for high stability of iron(III) chelates do not form satisfactory redox catalysts. Ligands that form suitable iron complexes as catalysts have both oxygen and nitrogen donors. All complexes investigated are readily reoxidized from the ferrous to the ferric chelate by air.

Key words: iron chelates, stability constants, redox potentials, hydrogen sulfide, redox catalysts.

Résumé : L'utilisation d'un système de chélate Fe(III)/Fe(II) pour l'enlèvement et l'oxydation du H_2S (en S) contenu dans une grande variété de sources de gaz aigres impose plusieurs limitations sur la nature du chélate de fer à utiliser comme catalyseur rédox. Pour que le H_2S soit absorbé efficacement à partir du gaz qui barbote dans la solution de catalyseur, il faut que celle-ci soit neutre ou légèrement alcaline. La stabilité du chélate de fer(III) doit être suffisamment élevée pour que le $Fe(OH)_3$ ne précipite pas au pH utilisé. Il faut aussi que la stabilité du chélate de fer(II) soit suffisamment élevée pour prévenir la précipitation du FeS à partir du mélange réactionnel. La différence dans les stabilités des chélates Fe(III) et Fe(II) doit être suffisamment basse pour que la forme Fe(III) puisse être réduite par HS^- et que le chélate Fe(III) puisse être régénéré par aération de la solution à un pH alcalin. Cette étude a conduit à un résultat inattendu; les agents chélatants développés pour donner des chélates de Fe(II) de grand stabilité ne donnent pas de catalyseurs rédox satisfaisants. Les coordinats qui forment des complexes de fer appropriés comme catalyseurs comportent à la fois des oxygènes et des azotes comme donneurs. Tous les complexes examinés peuvent facilement être réoxydés en chélate ferrique sous l'action de l'air.

Mots clés : chélates de fer, constantes de stabilité, potentiels rédox, sulfure d'hydrogène, catalyseurs rédox.

[Traduit par la rédaction]

Introduction

Iron(III) chelate systems are used as catalysts for the removal of H_2S from various gas streams including natural gas and for the oxidation of H_2S to S_8 by air. The reaction is usually carried out in two steps. In the absorber, H_2S is absorbed from the gas by a neutral or mildly alkaline solution of the catalyst and is oxidized by the ferric chelate to sulfur, S_8, which is eventually removed by filtration or other means, while the catalyst is converted to the ferrous form of the complex. The reduced catalyst is then oxidized by air in a separate part of the apparatus, called the oxidizer. In most cases the catalyst used commercially is an iron(III)/iron(II) chelate, and the chelating agent is an aminopolycarboxylic acid, such as NTA (nitrilotriacetic acid), EDTA (ethylenediaminetetraacetic acid), or HEDTA (*N*-hydroxyethylethylenediamine-*N,N′,N″*-triacetic acid), but such information is for the most part proprietary. The use of iron chelates of aminopolycarboxylic acids as catalysts in this process is covered by a number of patents, only a few of which are cited here (1–3).

Significant operating costs are incurred in the process due to the oxidation and eventual loss of the chelating ligand, which then has to be continuously replenished. The oxidation is probably a radical reaction, and two papers describing this problem in detail have been published (4, 5). This paper describes the chelating agents that form iron(III)/iron(II) chelate systems that promise to be effective catalysts for hydrogen sulfide oxidation. The choice of chelating agent is controlled by the conditions required for carrying out an efficient industrial process. The questions involved in the possible oxidative degradation of the chelating agent are not addressed. Such studies would require a separate, in-depth, study of the oxidation of the iron chelates involved.

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A.E. Martell,[1] R.J. Motekaitis, D. Chen, and R.D. Hancock. Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, U.S.A.
D. McManus. Wheelabrator Clean Air Systems, Inc., Plainfield, Illinois 60544, U.S.A.

[1] Author to whom correspondence may be addressed. Telephone: (409) 845-2011. Fax: (409) 845-4719.

Fig. 1. Plot of log K_1 for complexes of Fe^{2+} against log K_1 for the corresponding complexes of Fe^{3+}. This type of diagram shows the relative preference of Fe^{+3} for the harder ligands containing negative oxygen donors (○) compared to the softer ligands containing a mixture of nitrogen and oxygen donors (●).

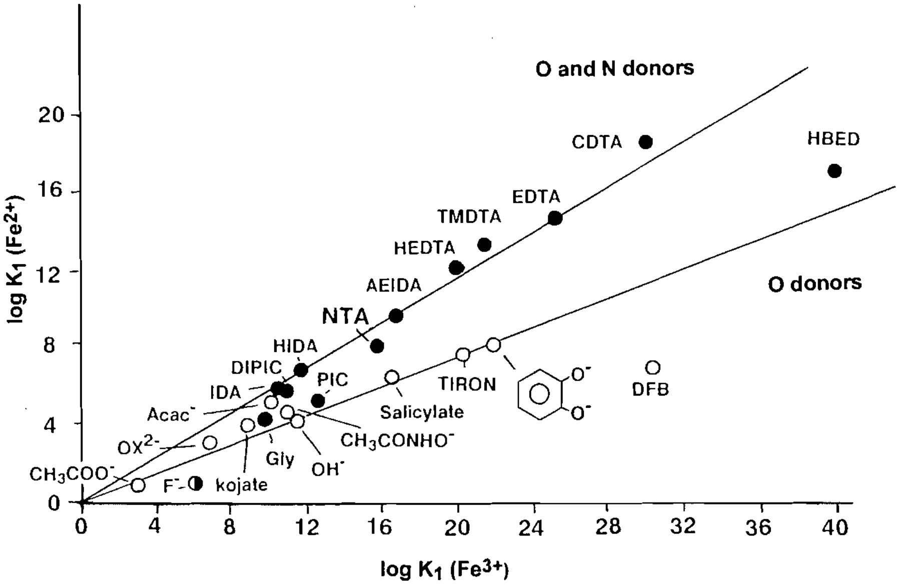
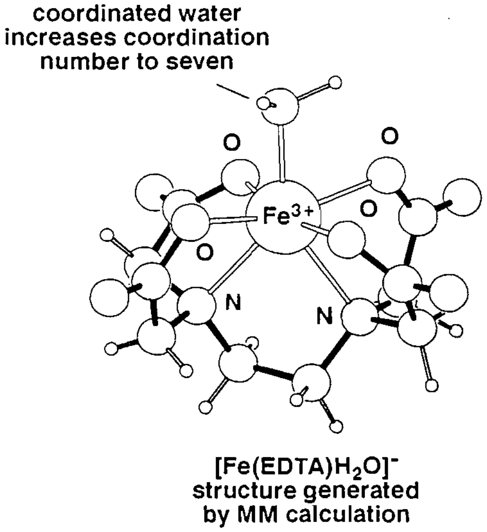


Fig. 2. Structure of Fe(II) complex of EDTA generated by Molecular Mechanics calculation and the program SYBYL.



Iron chelating ligands

In Fig. 1 are plotted the log equilibrium constants (formation constants) of 24 ligands with ferric and ferrous ions. The equilibrium constants used are for one mole of ligand per mole of ferric ion or ferrous ion. Since the scales of the ordinate and abscissa are the same, it is seen that a change in the nature and number of donor groups increases the stabilities of the ferric complexes much more than the ferrous complexes. Also, since the Fe^{3+} is a small hard acid (on the HSAB scale) (6, 7) it prefers to coordinate to an oxygen donor ligand with negative oxygen donor groups such as hydroxamate, phenolate, and catecholate donor oxygens. Where the ligand has some of the softer nitrogen donors, the stability of the ferrous chelate increases with basicity, but not as much as that of the ferric chelate. Thus the data in Fig. 1 seem to divide into two groups: those with ligands having only oxygen donors, with a high ratio of Fe(III)/Fe(II) stabilities, and those with both oxygen and nitrogen donors, with a lower ratio of Fe(III)/Fe(II) stability constants. The factors governing the stabilities of metal chelates have been described in detail (8, 9).

An important consideration is the coordination number of the metal ion, since the most stable complexes will be formed when the number of donor atoms of a ligand matches the requirement of the metal ion, provided of course that the donor atoms are sterically available to combine with the metal ion. Most of the complexes of Fe(II) and Fe(III) are octahedral, with a coordination number of six for a metal ion, matched by the coordinating donor groups supplied by a hexadentate ligand. Some complexes of the Fe^{3+} ion, however, are seven-coordinate, probably due in part to steric problems associated with the ligand. To appreciate such steric effects, MM calculations were carried out using the MM program SYBYL (10). The Fe(III) was modeled using the TAFF force field (10), with ideal Fe—O and Fe—N bond lengths of 2.00 and 2.38 Å, respectively, and Fe—O and Fe—N force constants of 100 kcal, mol^{-1} $Å^{-1}$. The angle bending force constants around the Fe, which are the N-Fe-N, N-Fe-O, and O-Fe-O angle bending force constants, were set to zero, and the geometry was generated by van der Waals repulsion between the donor atoms. Trial coordinates for the MM calculations were either taken from crystal structures, or were generated with the model-building facility of SYBYL. The resulting coordinates were plotted with PLUTON (11). Figure 2 shows the results of this molecular mechanics simulation of the Fe(III) chelate of EDTA in aqueous solution. The seven-coordinate structure agrees well with the crystal structure described earlier for the Fe(III)–EDTA chelate (12).

Because the absorber solution must be neutral or mildly alkaline, the possible precipitation of FeS and of $Fe(OH)_3$ are important considerations. Since the solubility product of FeS is $10^{-18.1}$ (13), it seems that FeS would precipitate if the concentration of $[Fe^{2+}]$ exceeds $10^{-9.2}$ (assuming $[HS^-]$ to be 10^{-3} M and taking $\log K_2^a$ of H_2S as 14.3; the solubility product of FeS is obtained from the displacement equilibrium constant $\log [M][H_2S]/[H^+]^2 = 3.0$). This places a lower limit on the stability constant of the ferrous chelate of the chelating agent selected. Similarly, if the solubility product of $Fe(OH)_3$ is $10^{-38.6}$ (14), it can be shown that $Fe(OH)_3$ would precipitate at pH 8.5 if the concentration of ferric ion is greater than $10^{-22.9}$ M. Thus the stability of the Fe(III) chelate must be higher than that which would allow the precipitation of Fe(III) as $Fe(OH)_3$ (in other words the pM (−log [M]) must be higher than 22.9).

In this paper the pM (−log [M]) of a metal ion is calculated for a metal buffer system in which there is an equal amount of the free chelating agent and metal chelate. Most metal chelates described below have 1:1 stoichiometry of metal ion M to chelating agent L; thus the stability constant $K = [ML]/[M][L]$. When $[L] = [ML]$, $\log K = -\log [M]$ and the analogy to a hydrogen ion buffer is complete. When the ligand:metal stoichiometry is 2:1 or 3:1, the excess free ligand necessary to form a metal buffer solution is proportionally higher. The excess free ligand used in this paper is an equivalent amount (100%) of that needed to form the metal complex.

The standard reduction potential E_0 of ferric to ferrous ion under standard conditions is +0.770 V (15). Since pM is −log [M], the half cell for the reduction of iron at pH 8.5 in the presence of 100% excess ligand is

$$[1]\quad \begin{aligned} E &= 0.770 + 0.059\,(\mathrm{pM}\,(\mathrm{Fe(II)}) - \mathrm{pM}\,(\mathrm{Fe(III)})) \\ E &= 0.770 - 0.059\,\Delta\,\mathrm{pM} \end{aligned}$$

For the reduction of sulfur, the reaction is

$$S(s) + 2H^+ + 2e^- \rightleftharpoons H_2S$$

and the standard reduction potential is +0.141 V (15).

The above equation is written in terms of HS^- since the latter is virtually the only form at pH 8.5. Since the first dissociation constant of H_2S is $10^{-6.82}$ (14)

$$E = E_0 - 0.0295 \log [H_2S]/[H^+]^2$$

$$[H_2S] = 10^{6.82}[H^+][HS^-]$$

$$E = 0.141 - 0.0295 \log 10^{6.82}\,[HS^-]/10^{-8.5}$$

Assume that $[HS^-]$ is approximately 10^{-3} M, a reasonable concentration.

$$E = 0.141 - 0.0295\,(6.82 - 3 + 8.5)$$

$$E = -0.223$$

For the overall reaction the reduction potential of the iron chelate and the oxidation potential of HS^- are employed:

$$[2]\quad \begin{aligned} E &= 0.770 - 0.059\,\Delta\,\mathrm{pM} + 0.223 \\ E &= 0.993 - 0.059\,\Delta\,\mathrm{pM} \end{aligned}$$

For the two-electron redox reaction at pH 8.5 the conditional equilibrium constant may now be calculated.

$$[3]\quad \log K_c = (0.993 - 0.059\,\Delta\,\mathrm{pM})/0.0295$$

Thus the values of the conditional constants K_c for the equilibrium

$$2Fe^{III}L + HS^- \rightleftharpoons 2Fe^{II}L + H^+ + S(s)$$

were calculated for Tables 1 and 2, for pH 8.5, 100% excess ligand, and assuming the concentration of HS^- to be 10^{-3} M.

The conditions used for Tables 1 and 2, and which apply to the conditional equilibrium constant K_c, specify pH 8.5, which corresponds to the pH used in the Wheelabrator "Low-Cat" process. The use of a much lower pH, such as 7.0, used in the Dow "Sulferox" system, would result in much lower S^{2-} and OH^- concentrations, and therefore the precipitation of FeS and $Fe(OH)_3$ would occur less readily. Thus, chelating agents labeled in Table 1 with (S) and (OH) and in Table 2 as (borderline), would be satisfactory. The rate of absorption of H_2S, however, would be slower, and a larger absorber vessel would be needed.

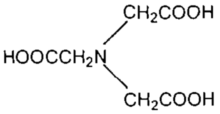
Another condition that may be employed for this process is the use of a lesser amount of excess ligand. The reduction of 100% excess ligand to 10% excess would reduce the pM value of the catalyst system by an order of magnitude. This change could be tolerated better in the low pH process, where the demands on the chelating agent to keep the iron in solution are not so stringent.

Because certain aminopolycarboxylate chelates are now in use commercially to form the iron chelate catalysts for this process, it seems appropriate to compare these systems with other aminopolycarboxylates. Table 1 compares 10 aminopolycarboxylates for which the stabilities meet the requirements for the oxidation of H_2S to S_8 at pH 8.5 and 10^{-3} M $[HS^-]$. The structures and names of the ligands are indicated in Plate 1. It is seen that the reaction is favorable for all ligands listed in Table 1 with conditional constants that vary between 10^8 and 10^{24}. It is seen that TMDTA and EGTA are unsatisfactory ligands because they do not prevent the precipitation of $Fe(OH)_3$ at pH 8.5. Also, NTA calculates out as a marginal ligand with respect to both FeS and $Fe(OH)_3$ precipitation. The fact that it is being successfully used in industrial applications indicates that the operating conditions are at least a little different from those used in the calculations. In some cases an additive is used to increase the complexation of iron(III).

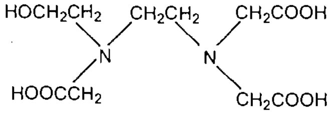
A larger variety of chelating agents are listed in Table 2, including ligands with very basic oxygen donors designed to form very stable Fe(III) chelates. The structures and names of these ligands are given in Plate 2. It is noted that the stabilities of the Fe(II) complexes of four of these ligands have not been measured. Their values are estimated (extrapolated) from the stability constants of other transition divalent metal complexes with the same ligands. The accuracy of this approximation is considered adequate. It is seen in Table 2 that the stabilities of the Fe(III) chelates of TETA and ACAC are not high enough to prevent precipitation of $Fe(OH)_3$. The most

Plate 1.

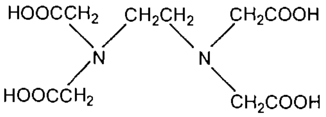
Aminopolycarboxylic Acids: Names, Acronyms, Formulas



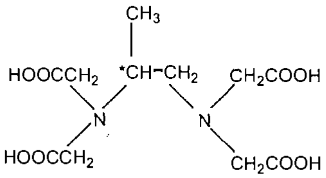
Nitrilotriacetic acid, H_3L (NTA)



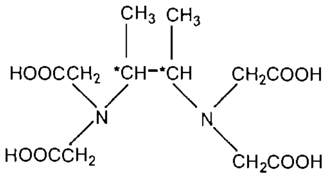
N(-2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid, H_3L (HEDTA)



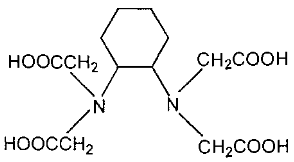
Ethylenedinitrilotetraacetic acid, H_4L (EDTA)



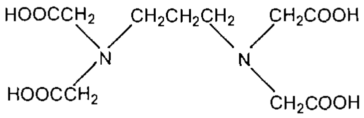
Racemic-propylenediaminetetraacetic acid, H_4L (PDTA)



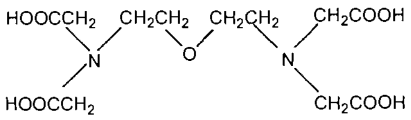
Racemic-1,2-dimethylethylenediaminetetraacetic acid, H_4L (DMEDTA)



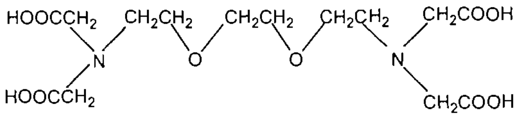
trans-1,2-diaminocyclohexanetetraacetic acid, H_4L (CDTA)



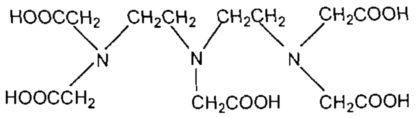
Trimethylenediminetetraacetic acid H_4L (TMDTA)



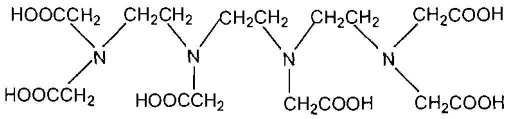
Oxybis(ethylenenitrilo)tetraacetic acid H_4L (EEDTA)



Ethylenebis(oxyethylenenitrilo)tetraacetic acid, H_4L (EGTA)



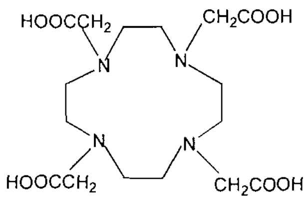
Diethylenetriaminepentaacetic acid, H_5L (DTPA)



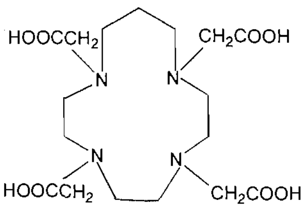
Triethylenetetraminehexaacetic acid, H_6L (TTHA)

Plate 2.

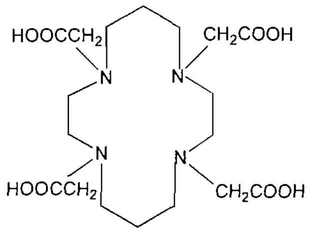
Miscellaneous Chelating Agents: Names, Acronyms, Formulas



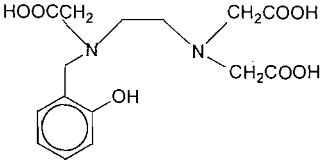
1,4,7,10-tetraazacyclododecane-
N,N',N'',N'''-tetraacetic acid, H_4L (DOTA)



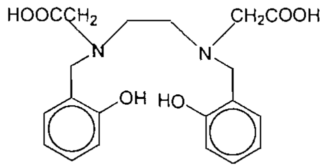
1,4,7,10-tetraazacyclotridecane-
N,N',N'',N'''-tetraacetic acid, H_4L (TRITA)



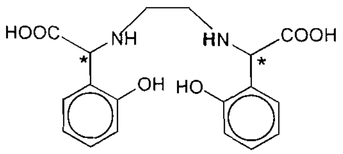
1,4,8,11-tetraazacyclotetradecane-
N,N',N'',N'''-tetraacetic acid, H_4L (TETA)



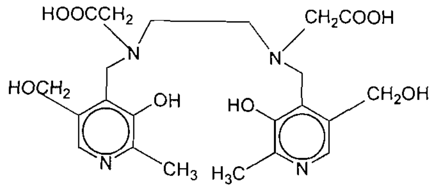
N-(2-hydroxybenzylethylenediamine-
N,N',N'-triacetic acid, H_4L (HBET)



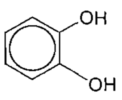
N,N'-bis(20hydroxybenzyl)ethylenediamine-
N,N'-diacetic acid, H_4L (HBED)



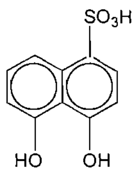
Racemic-ethylene-N,N'-bis(2-
hydroxyphenylglycine, H_4L (EHPG)



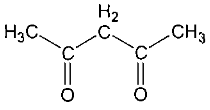
N,N'-bis(2-methyl-3-hydroxy-5-hydroxymethyl
4-pyridylmethyl)ethylenediamine-N,N'-diacetic
cid, H_4L (PLED



1,2-dihydroxybenzene, catechol
H_2L (CAT)



1,8-dihydroxynaphthalene-4-sulfonic acid
H_3L (DHNS)



Acetylacetone, 2,4-pentanedione
HL (ACAC)

Table 1. Stability constants of Fe(II) and Fe(III) chelates, pM's, and log K_c's[a] for the aminopolycarboxylic acids.

	Log K_{ML}[b]		pM[c]				
	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}	ΔpM	$E(Fe^{3+} \rightarrow Fe^{2+})$[d]	Log K_c[a]
NTA	8.05	15.9	8.0 (S)[e]	20.8 (OH)[e]	12.8	0.013	7.98
HEDTA	12.2	19.8	10.9	23.7	12.8	0.013	7.98
EDTA	14.30	25.10	12.6	25.2	12.6	0.025	8.38
PDTA	15.50	26.0	13.1	23.6	10.5	0.149	12.58
DMEDTA	17.8	28.05	14.0	25.0	11.0	0.119	11.56
CDTA	18.90	30.00	15.0	26.2	11.2	0.107	11.16
TMDTA	13.46	21.61	11.4	19.6 (OH)[e]	8.2	0.285	17.17
EEDTA	14.20	24.7	12.7	23.2	10.5	0.149	12.58
EGTA	11.20	20.50	10.4	19.1 (OH)[e]	8.7	0.255	16.16
DTPA	16.40	28.00	14.2	25.6	11.4	0.096	10.78
TTHA	17.00	26.80	18.9	23.7	4.8	0.486	23.97

[a] K_c are the conditional constants for the reaction $2\,Fe^{III}L + HS^- \rightleftharpoons 2Fe^{II}L + H^+ + S(s)$ at pH 8.5 and HS^- taken as 10^{-3} M.

[b] Log K_{ML} taken from NIST Critical Stability Constant Database No. 46.

[c] For 100% excess ligand, 10^{-2} M metal chelate.

[d] E for reduction of ferric to ferrous ions taken from pM values of the metal ions and the equation $E = 0.770 - 0.059 \log [Fe^{2+}]/[Fe^{3+}]$.

[e] (S) and (OH) indicate propensity for FeS and $Fe(OH)_3$ formation, respectively.

Table 2. Stability constants of Fe(II) and Fe(III) chelates, pM's, and log K_c's[a] for other ligands.

	Log K_{ML}[b]		pM[c]				
	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}	ΔpM	$E(Fe^{3+} \rightarrow Fe^{2+})$[d]	log K_c[a]
DOTA	20.22	39.40	16.3	35.4	19.1	−0.360	−4.63 (weak)
TRITA	17.6	27.50	13.5	23.4	9.9	+0.184	13.76
TETA	13.32	26.50	9.5	22.6 (OH)[e]	13.1	−0.005	7.37
HBET	15.0 (est.)	32.02	10.9	27.9	17.0	−0.236	−0.44 (weak)
HBED	22.7 (est.)	39.01	15.7	32.1	16.4	−0.200	0.78 (weak)
EHPG	20.6 (est.)	35.54	14.2	29.1	14.9	−0.111	3.89 (borderline)
PLED	17.9 (est.)	30.80	13.7	26.6	12.9	+0.007	7.78
CAT	8.3	20.4	4.4 (S)[e]	25.3	20.9	−0.466	−8.22 (weak)
DHNS	8.99	19.84	7.0 (S)[e]	25.5	18.5	−0.324	−3.41 (weak)
ACAC	5.07	9.30	6.9 (S)[e]	21.3 (OH)[e]	14.4	−0.082	4.77

[a] K_c are the conditional constants for the reaction $2\,Fe^{III}L + HS^- \rightleftharpoons 2Fe^{II}L + H^+ + S(s)$ at pH 8.5 and HS^- taken as 10^{-3} M.

[b] Log K_{ML} taken from NIST Critical Stability Constant Database No. 46.

[c] For 100% excess ligand, 10^{-2} M metal chelate.

[d] E for reduction of ferric to ferrous ions taken from pM values of the metal ions and the equation $E = 0.770 - 0.059 \log [Fe^{2+}]/[Fe^{3+}]$.

[e] (S) and (OH) indicate propensity for FeS and Fe(OH)3 formation, respectively.

remarkable feature of the data in Table 2 is that the chelating agents that form very stable Fe(III) chelates are not suitable for the oxidation of H_2S to S_8. Any ligand that produces a conditional constant lower than 10^4 is considered too weak an oxidizing agent. This behavior may be rationalized on the basis of the fact that the Fe(III) chelate is very stable, compared to the Fe(II) chelate, and the metal ion therefore prefers to remain in the ferric form. A successful ligand is one that stabilizes the Fe(II) form sufficiently so that it is only moderately less stable than the Fe(III) chelate. The best measure of the relative effects of the ligand on these metal ions is the difference in pM values, since pM takes into account environmental considerations such as pH and concentration.

The reoxidation of the ferrous to the ferric chelate by air, which takes place in the oxidizer vessel, involves the following reaction:

$$4Fe^{II}L + O_2 + 4H^+ \rightleftharpoons 4Fe^{III}L + 2H_2O$$

and the equilibrium constant, in the form of a concentration constant, is

$$[4]\quad K' = \frac{[\mathrm{Fe^{III}L}]^4}{[\mathrm{Fe^{II}L}]^4[\mathrm{H^+}]^4\,\mathrm{P_{O_2}}}$$

where all solution species are expressed as molar concentration, except the concentration of O_2 which is expressed as partial pressure.

If one takes pH 8.5 as the operating pH and employs 0.20 as the partial pressure of oxygen in air, and substitutes these values in eq. [4], one obtains an equation for the corresponding conditional constant.

$$K'([\mathrm{H^+}]^4)0.2 = \frac{[\mathrm{Fe^{III}L}]}{[\mathrm{Fe^{II}L}]}$$

$$K'_c = K'(10^{-34})(0.2) = \frac{[\mathrm{Fe^{III}L}]}{[\mathrm{Fe^{II}L}]}$$

$$\log K'_c = \log K' - 34.7 = \log \frac{[\mathrm{Fe^{III}L}]}{[\mathrm{Fe^{II}L}]}$$

The emf corresponding to the overall reaction can be considered as the sum of the emf's of the half reactions for the oxidation of the iron chelate and the reduction of O_2. For the latter,

$$\mathrm{O_2 + 4H^+ + 4e \rightarrow 2H_2O}$$

E is +1.229 V for unit molality of H^+ and unit partial pressure of O_2 (15).

$$E = 1.229 - 0.01479 \log 1/(0.2) - 0.059\,(8.5) = 0.727$$

For the whole reaction, E'_c is therefore:

$$[5]\quad E'_c = E(\mathrm{Fe^{II}L \rightarrow Fe^{III}L}) + 0.727\ \mathrm{V}$$

Therefore, K'_c can be expressed by the following:

$$[6]\quad \log K'_c = E'_c/0.01479$$

The values of $\log K'_c$ are given in Table 3 for oxidation of the ferrous chelates of the 21 systems described in Tables 1 and 2. It seems that, for all the chelate systems considered, whether or not they are satisfactory for the oxidation of H_2S in the absorber, the equilibrium constants for the oxidation reactions are very positive, and the oxidation of all the ferrous chelates to the ferric form is highly favored. The authors have checked the use of several iron chelates as catalysts in the oxidation of H_2S to S by air and have not encountered any difficulties due to slow kinetics. Although all phases of the reaction were adequately rapid, the reoxidation of the ferrous to the ferric chelate seemed to be the slower part of the process. The slowest part of the reoxidation is the dissolution of oxygen from air to the aqueous phase. This part of the process may be maximized by the use of an appropriate gas–liquid contacting device.

Although all the constants listed in Table 3 are highly positive, they do not provide information on the kinetics of reaction, except that the oxidation step is highly favored.

Table 3. Conditional equilibrium constants[a] for the oxidation of ferrous chelates to the ferric form by air in the presence of 100% excess ligand at pH 8.5.

Ligand	$E(\mathrm{Fe^{2+} \rightarrow Fe^{3+}})$[b]	E_c (reaction)	$\log K'_c$[a,c]
NTA	−0.013	0.714	48.3
HEDTA	−0.013	0.714	48.3
EDTA	−0.025	0.762	47.5
PDTA	−0.149	0.578	39.1
DMEDTA	−0.119	0.608	41.1
CDTA	−0.107	0.620	41.9
TMDTA	−0.285	0.442	29.9
EEDTA	−0.149	0.578	39.1
EGTA	−0.255	0.472	31.9
DTPA	−0.096	0.631	42.7
TTHA	−0.486	0.241	16.3
DOTA	+0.360	1.087	73.5
TRITA	−0.184	0.543	36.7
TETA	+0.005	0.732	49.5
HBET	+0.236	0.963	65.1
HBED	+0.200	0.927	62.7
EHPG	+0.111	0.838	56.7
PLED	+0.007	0.720	48.7
CAT	+0.466	1.193	80.7
DHNS	+0.324	1.051	71.06
ACAC	+0.082	0.809	54.7

[a] Equilibrium constant for the reaction: $\mathrm{4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+}L + 2H_2O}$ at pH 8.5 and P_{O_2} of 0.20 (air) in the presence of 100% excess ligand.

[b] Oxidation potential of the Fe(II)/Fe(III) chelate couple in the presence of 100% excess ligand.

[c] Calculated from the equation $E_c = 0.059/n \log K_c$.

Conclusions

To form Fe(II)/Fe(III) chelates that are useful as catalysts for the oxidation of H_2S to S, a chelating agent must:

1. Function in the neutral or mildly alkaline pH range to rapidly absorb H_2S gas.
2. Form sufficiently stable Fe(III) chelates that are not converted to $Fe(OH)_3$ at alkaline pH.
3. Form sufficiently stable Fe(II) chelates to prevent precipitation of FeS from alkaline solution.
4. The Fe(III) chelates are generally more stable than the Fe(II) chelates, the ΔpM values varying between 5 and 13 for the amino carboxylic acids and up to 21 for the other ligands. If the Fe(III) chelate is too stable relative to the Fe(II) chelate (ΔpM > 16), the catalyst is ineffective. (The chelate prefers to remain in the Fe(III) state.)
5. Favorable redox reactions are associated with conditional constants that vary over a wide range of numerical values. At pH 8.5 and $[\mathrm{HS^-}]$ of 10^{-3} M, the conditional constant may vary between 10^4 and 10^{24}.
6. Because all the ligands listed in Tables 1 and 2, and in Fig. 1, have Fe(III) stability constants that are higher than those of Fe(II), oxidation of the Fe(II) chelate to the Fe(III) chelate by air is a highly favored reaction. While there are ligands that stabilize the ferrous form more than the ferric chelates, such ligands are not useful in this process and are not discussed here.

Glossary

ACAC	acetylacetone, 2,4-pentanedione
AEIDA	*N*-(2-aminoethyl)iminodiacetic acid
CAT	1,2-dihydroxybenzene, catechol
CDTA	*trans*-1,2-diaminocyclohexanetetraacetic acid
CH_3CONHO^-	acethydroxamic acid anion
CH_3COO^-	acetic acid anion
DFB	desferriferrioxamine-B
DHNS	1,8-dihydroxynaphthalene-4-sulfonic acid
DIPIC	dipicolinic acid
DMEDTA	*racemic*-1,2-dimethylethylenediaminetetraacetic acid
DOTA	1,4,7,10–tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid
DTPA	diethylenetriaminepentaacetic acid
EDTA	ethylenedinitrilotetraacetic acid, ethylenediamine-tetraacetic acid
EEDTA	oxybis(ethylenenitrilo)tetraacetic acid
EGTA	ethylenebis(oxyethylenenitrilo)tetraacetic acid
EHPG	*racemic*-ethylene-*N*,*N*′-bis(2-hydroxyphenylglycine)
Gly	glycine
HBED	*N*,*N*′-bis(2-hydroxybenzyl)ethylenediamine-*N*,*N*′-diacetic acid
HBET	*N*-(2-hydroxybenzyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid
HEDTA	*N*-(2-hydroxyethyl)ethylenediamine,*N*,*N*′,*N*′-triacetic acid
HIDA	*N*-(2-hydroxyethyl)iminodiacetic acid
IDA	iminodiacetic acid
Kojate	kojic acid anion
NTA	nitrilotriacetic acid
Ox^{2-}	oxalic acid anion
PDTA	*racemic*-propylenediaminetetraacetic acid
PIC	picolinic acid
PLED	*N*,*N*′-bis(2-methyl-3-hydroxy-5-hydroxymethyl-4-pyridylmethyl)ethylenediamine-*N*,*N*′-diacetic acid
TETA	1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid
Tiron	3,5-disulfocatechol
TMDTA	trimethylenediaminetetraacetic acid
TRITA	1,4,7,10-tetraazacyclotridecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid
TTHA	triethylenetetraminehexaacetic acid

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