# Solution Chemistry of *NN'*-Ethylenebis(salicylidenimeinato)iron(III). Part 2.† Formation Equilibria of μ-Oxo-bis[*NN'*-ethylenebis(salicylideneiminato)iron(III)] and Catecholato[*NN'*-ethylenebis(salicylideneiminato)]ferrate(III)

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The complex $[Fe(salen)]^+$ [$H_2salen$ = *NN'*-ethylenebis(salicylideneimine)] can dimerize in dimethyl sulphoxide–$H_2O$ (80 : 20 w/w) solution according to the following equation: $2\,[Fe(salen)]^+ + H_2O \overset{K_D}{\rightleftharpoons} [\{Fe(salen)\}_2O] + 2\,H^+$. Although the μ-oxo-complex has been known for some time, this equilibrium has not been studied up to now; the equilibrium constant, $K_D = (5.00 \pm 0.05) \times 10^{-13}$ mol dm$^{-3}$ (0.1 mol dm$^{-3}$ $KClO_4$, 25 °C). $[Fe(salen)]^+$ interacts in solution with catechol ($H_2cat$) to give $[Fe(salen)(cat)]^-$. We have determined the complex formation constant, $[Fe(salen)]^+ + cat^{2-} \overset{K}{\rightleftharpoons} [Fe(salen)(cat)]^-$, $K = (4.79 \pm 0.02) \times 10^{14}$ dm$^3$ mol$^{-1}$ (0.1 mol dm$^{-3}$ $KClO_4$, 25 °C). In this complex, $cat^{2-}$ is co-ordinated as a bidentate ligand. This fact implies a marked structural change in the $salen^{2-}$ ligand, from the normal planar configuration to a very distorted one. There is no kinetic hindrance to this change, as shown by the fast formation equilibrium, but the distorted anion causes reduced stability compared to the planar anion.

Iron is the most important transition element in biological systems, forming part of many metalloproteins and metalloenzymes.[1] Although the active sites of heme proteins are well characterized, less is known about non-heme proteins. Recently, some iron dioxygenases such as pyrocatechase have received great attention.[2] These enzymes catalyze the catechol (benzene-1,2-diol) oxidation by dioxygen to give *cis*-muconic acid. Although the active site has been investigated in detail, it is only known that it contains a high-spin iron(III) atom linked to two tyrosinate groups.[3] So far, the other metal-ion ligands have not been identified. On the other hand, formation of an enzyme-substrate complex with catechol has been evidenced by different physical techniques but its nature is not yet understood.[3]

Que [2] used the complex $[Fe^{III}(salen)(O_2CMe)]$ [$H_2salen$ = *NN'*-ethylenebis(salicylidenimine)] as a model for the active site of these non-heme iron dioxygenases and isolated a catecholate complex, K[Fe(salen)(cat)] ($H_2cat$ = catechol). Although its molecular structure has not yet been determined, the corresponding complex, [Fe(salphen)(Hcat)] [$H_2salphen$ = *o*-phenylenebis(salicylideneimine)] is known;[4] *X*-ray diffraction studies reveal the unusual presence of a unidentate $Hcat^-$ ligand. On the basis of the similarity of the spectral properties displayed by both compounds it has been suggested [2] that the $cat^{2-}$ anion is also unidentate in $[Fe(salen)(cat)]^-$. However, this is not obvious since although $salphen^{2-}$ has a rigid structure which prevents co-ordination of a bidentate ligand, $salen^{2-}$ is much more flexible. *X*-Ray studies of [Co(salen)(acac)] [5] (Hacac = acetylacetone) and [Co(salen)(bzac)] [6] (Hbzac = benzoylacetone) reveal the presence of a very distorted $salen^{2-}$ ligand, allowing the co-ordination of a bidentate β-diketonate ligand.

Hendrickson and co-workers [7] isolated monomeric complexes of $Fe^{III}$–salen with different semiquinone ligands and suggested that the metal ion was six-co-ordinate. Nakamura *et al.*[8] isolated and characterized a series of $Fe^{III}$(salen) complexes with bidentate ligands such as acetylacetone, salicylaldehyde, *etc.*, to find that in the solid state these complexes have a *cis*-β octahedral structure.

In the preceding paper we studied the formation of $[Fe(salen)]^+$ in dmso–$H_2O$ (80 : 20 w/w) (dmso = dimethyl sulphoxide) solution. In the present work we investigate the formation of catecholate complexes of $[Fe(salen)]^+$ in the same solvent, as well as the formation of the dimeric oxo-complex $[\{Fe(salen)\}_2O]$.

## Experimental

Potentiometric and spectrophotometric measurements were performed as reported earlier.[9] 0.1 mol dm$^{-3}$ KOH was used as a titrant except when a more concentrated base solution was required, for which tetrabutylammonium hydroxide, much more soluble in dmso–$H_2O$ (80 : 20), was used. All the solutions used in this work were prepared in this mixed solvent. Catechol (Merck, synthesis grade) was recrystallized by sublimation before use. Because of the catechol sensitivity to oxidation in basic medium, $O_2$ traces in the $N_2$ used as inert atmosphere were carefully eliminated.

The i.r. spectrum of $[\{Fe(salen)\}_2O]$ was recorded with a Pye Unicam SP2000 spectrophotometer. The C and N analyses were performed with a Coleman 33 elemental analyzer. For further details see Experimental section of the preceding paper.

*Synthesis of* $[\{Fe(salen)\}_2O]$.—The complex $[\{Fe(salen)Cl\}_2]$ (0.625 g) was dissolved in dmso–$H_2O$ (80 : 20) (15 cm$^3$) and 0.1 mol dm$^{-3}$ KOH (18 cm$^3$) in the same solvent was added with continuous stirring. The orange crystalline precipitate was filtered off and washed with a few cm$^3$ of solvent and then exhaustively with acetone. The crystals were oven-dried at 70 °C and stored in a $CaCl_2$ desiccator. The yield was almost quantitative (>96%) (Found: C, 58.0; Fe, 16.9; N, 8.5. Calc. for $C_{32}H_{28}Fe_2N_4O_5$: C, 58.2; Fe, 16.9; N, 8.5%). The diffuse reflectance and i.r. spectra of the obtained solid agreed with those reported in the literature.[10]

## Results

*Acidity Constants of Catechol in* dmso–$H_2O$ (80 : 20).—We titrated catechol solutions of different concentrations, $c_L$, by potentiometry. From the potentiometric data the protonation

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† Part 1 is ref. 9.

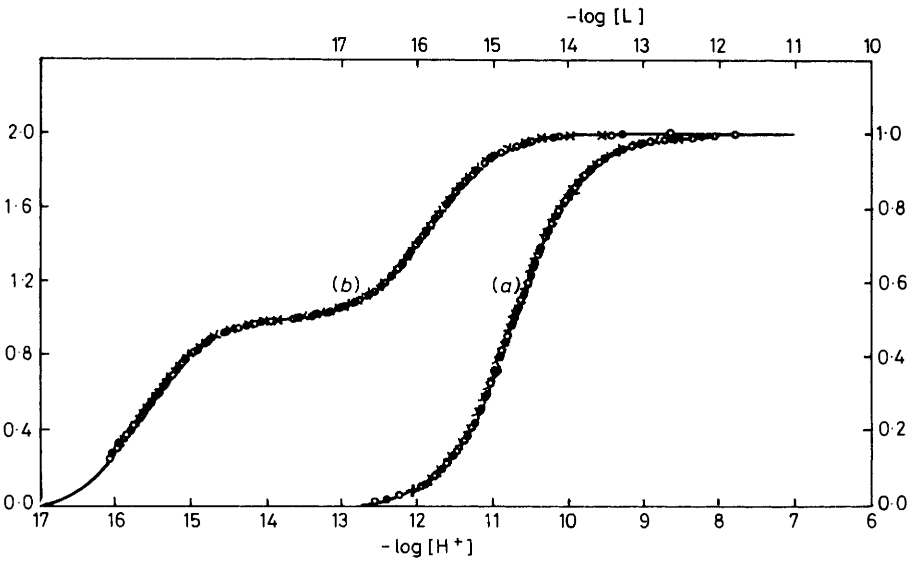

**Figure 1.** (*a*) Formation curve of [Fe(salen)(cat)]$^-$ : $c_M = 1.08 \times 10^{-3}$ (●), $3.23 \times 10^{-3}$ (○), and $5.87 \times 10^{-3}$ mol dm$^{-3}$ (×); $c_L : c_M = 10$. (*b*) Protonation curve of cat$^{2-}$ : $c_L = 1.32 \times 10^{-3}$ (●), $4.57 \times 10^{-3}$ (○), and $1.02 \times 10^{-2}$ mol dm$^{-3}$ (×)

curve $\bar{j}$ *versus* $-\log [H^+]$ was obtained (Figure 1). The overall proton association constants were computed from this curve; $\beta_{j1} = (3.71 \pm 0.02) \times 10^{15}$ and $\beta_{j2} = (2.30 \pm 0.03) \times 10^{27}$ (25 °C, 0.1 mol dm$^{-3}$ KClO$_4$). 90 Experimental points from three different experiments were used in the calculus. The curve calculated with the computed constants fitted perfectly the experimental points until $\bar{j} \geqslant 0.3$. For $\bar{j} < 0.3$ the hydrogen-ion concentration was too low (pH >16) and the electrode response was not completely satisfactory.[9]

*Formation Equilibria of* μ-*Oxo-bis*[NN′-*ethylenebis*(*salicylideneiminato*)*iron*(III)].—When KOH is added to a [Fe(salen)]$^+$ solution in dmso–H$_2$O (80 : 20) a colour change from red to orange occurs. The recorded spectra (Figure 2) displayed an isosbestic point which indicated two absorbing species in solution. Reaction was complete when one mole of OH$^-$ for each mole of [Fe(salen)]$^+$ had been added. The absorption spectrum of the orange solutions is identical to the reflectance spectrum of the solid [{Fe(salen)}$_2$O]. Therefore it is apparent that reaction (1) is taking place. The equilibrium constant, $K_D$, can be determined by potentiometry, using equation (2).

$$2\,[\text{Fe(salen)}]^+ + \text{H}_2\text{O} \overset{K_D}{\rightleftharpoons} [\{\text{Fe(salen)}\}_2\text{O}] + 2\,\text{H}^+ \quad (1)$$

$$K_D = ([\text{Fe}_2(\text{salen})_2\text{O}][\text{H}^+]^2)/[\text{Fe(salen)}^+]^2 \quad (2)$$

The concentrations of both complexes can be expressed as a function of [H$^+$], taking into account the mass balances of the system, and obtaining equation (3), where $c_M$ and $c_H$ are

$$\tfrac{1}{2}(c_M - c_H + [\text{H}^+] - K_w/[\text{H}^+]) = K_D\{(c_H - [\text{H}^+] + K_w/[\text{H}^+])/[\text{H}^+]\}^2 \quad (3)$$

the initial concentrations of [Fe(salen)]$^+$ and neutralizable hydrogen ions, respectively. We can write equation (3) as $Y = K_D X$. In a solution of known analytical concentrations the experimental measurements of [H$^+$] give the values of $X$ and $Y$.

Solutions of [Fe(salen)]$^+$ were titrated potentiometrically with KOH. The initial concentration, $c_M$, was varied in the range $1 \times 10^{-3}$—$5 \times 10^{-3}$ mol dm$^{-3}$. Because of the oxo-complex precipitation, higher concentrations could not be used. Potentiometric curves displayed a steep inflexion for a $c_B : c_M = 1$ ratio, in agreement with the spectrophotometric data. When plotting $Y$ *versus* $X$ a straight line which intercepts the origin was obtained (Figure 3). The slope gave the equilibrium constant, $K_D = (5.00 \pm 0.05) \times 10^{-13}$ mol dm$^{-3}$. In the calculus of this constant 70 experimental points from three independent experiments were used.

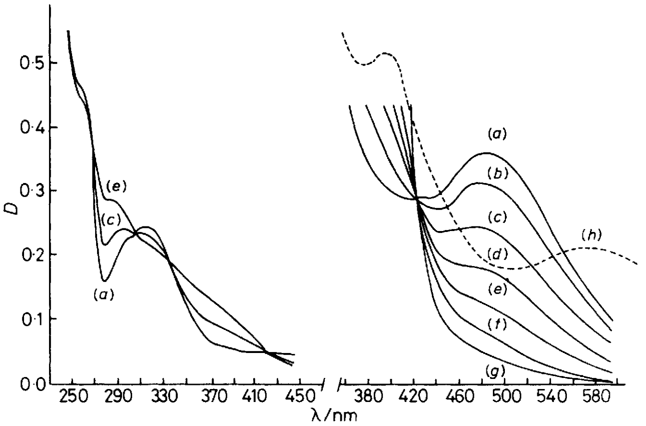

**Figure 2.** U.v.–visible absorption spectra of [Fe(salen)]$^+$ solutions ($c_M = 9.5 \times 10^{-5}$ mol dm$^{-3}$) with different $c_B : c_M$ ratios: (*a*) 0, (*b*) 0.2, (*c*) 0.4, (*d*) 0.6, (*e*) 0.75, (*f*) 0.85, and (*g*) 1.0. The spectra (*a*), (*c*), and (*e*) on the left were recorded with 0.2-cm instead of 1-cm cells. (*h*) Visible spectrum of a [Fe(salen)(cat)]$^-$ solution ($1.55 \times 10^{-4}$ mol dm$^{-3}$)

In the concentration range studied, the dimerization reaction was almost complete for pH $\geqslant$ 9 (Figure 4).

*Formation Study of the Complex* [Fe(salen)(cat)]$^-$.—When adding KOH to [Fe(salen)]$^+$ solutions containing catechol a colour change from red to green, due to [Fe(salen)(cat)]$^-$ formation, occurs. The absorption spectra display two bands at 575 (ε *ca.* $1.4 \times 10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$) and 396 (ε *ca.* $3.4 \times 10^3$) (Figure 2).

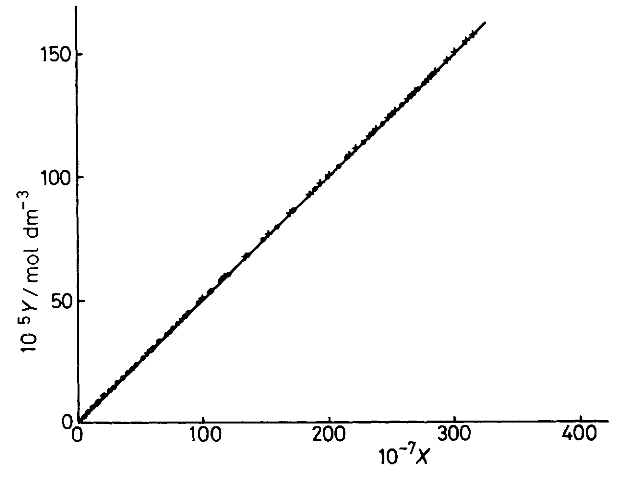

**Figure 3.** Plot of $Y = \frac{1}{2}(c_M - c_H + [H^+] - K_w/[H^+])$ *versus* $X = \{(c_H - [H^+] + K_w/[H^+])/[H^+]\}^2$ for a series of $[Fe(salen)]^+$ solutions with variable amounts of KOH: $c_M = 1.35 \times 10^{-3}$ (○), $3.12 \times 10^{-3}$ (●), and $3.96 \times 10^{-3}$ mol dm$^{-3}$ (×)

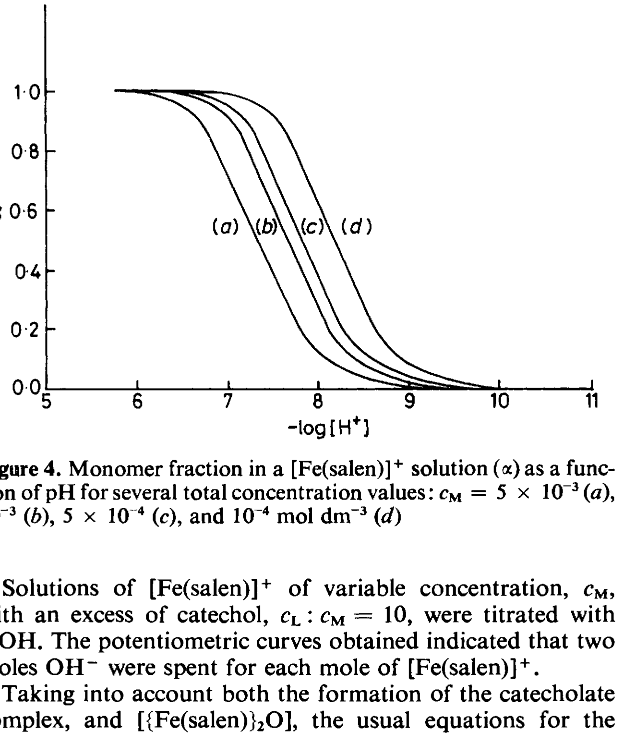

**Figure 4.** Monomer fraction in a $[Fe(salen)]^+$ solution (α) as a function of pH for several total concentration values: $c_M = 5 \times 10^{-3}$ (*a*), $10^{-3}$ (*b*), $5 \times 10^{-4}$ (*c*), and $10^{-4}$ mol dm$^{-3}$ (*d*)

Solutions of $[Fe(salen)]^+$ of variable concentration, $c_M$, with an excess of catechol, $c_L : c_M = 10$, were titrated with KOH. The potentiometric curves obtained indicated that two moles $OH^-$ were spent for each mole of $[Fe(salen)]^+$.

Taking into account both the formation of the catecholate complex, and $[\{Fe(salen)\}_2O]$, the usual equations for the degree of formation, $\bar{n}$, and for the free-ligand concentration can be modified as in equations (4) and (5).

$$\bar{n} = \frac{c_L - 1/\bar{j}(c_H - [H^+] + K_w/[H^+] + 2[\{Fe(salen)\}_2O])}{c_M - 2[\{Fe(salen)\}_2O]} \qquad (4)$$

$$[cat^{2-}] = \frac{c_L - \bar{n}(c_M - 2[\{Fe(salen)\}_2O])}{1 + \beta_{j1}[H^+] + \beta_{j2}[H^+]^2} \qquad (5)$$

In equations (4) and (5) the dimeric oxo-complex concentration at equilibrium appears. Fortunately, this concentration can be expressed as a function of $[H^+]$. Considering equation (2) and the mass balances equation (6) can be derived, where $x = 2[\{Fe(salen)\}_2O]^{\frac{1}{2}}$. The only acceptable solution of equation (6) is given by equation (7). From the potentiometric data, and using equations (7), (4), and (5) we obtained the formation curve, $\bar{n}$ *versus* $-\log[cat^{2-}]$ (Figure 1). By plotting $\bar{n}/(1 - \bar{n})$ *versus* $[cat^{2-}]$, a straight line which intercepts the origin is obtained. Its slope gives the formation constant $K = (4.79 \pm 0.02) \times 10^{14}$ dm$^3$ mol$^{-1}$ [equation (8)]. In

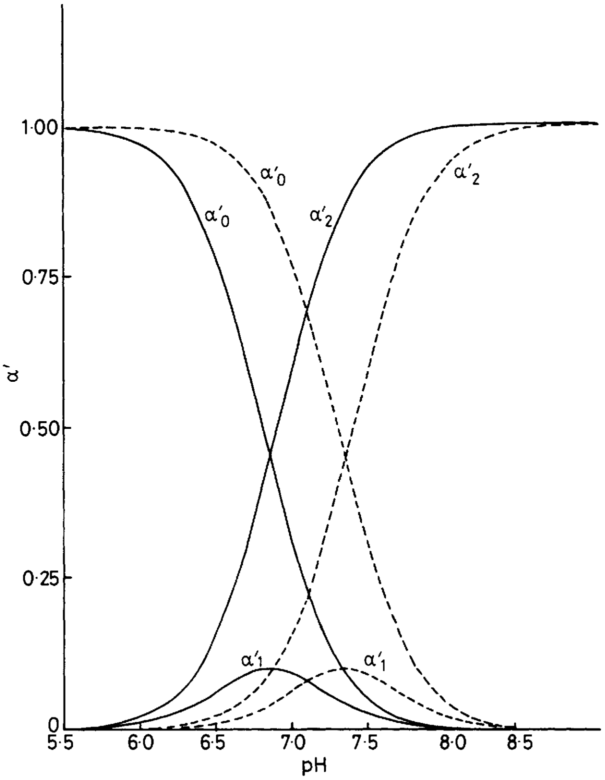

**Figure 5.** Distribution diagram (α′ *versus* pH) for the system $[Fe(salen)]^+$–$cat^{2-}$: $\alpha_0' = [Fe(salen)]^+$, $\alpha_1' = [\{Fe(salen)\}_2O]$, $\alpha_2' = [Fe(salen)(cat)]^-$ (α′ is the molar fraction of metal ion). Concentrations $c_M = 10^{-3}$, $c_L = 10^{-2}$ (——) and $c_M = 10^{-2}$, $c_L = 10^{-1}$ mol dm$^{-3}$ (– – –)

$$x^2 + ([H^+]/K_D^{\frac{1}{2}})x - \tfrac{1}{2}(2c_M - c_B - [H^+] + K_w/[H^+]) = 0 \qquad (6)$$

$$x = ([H^+]/2K_D^{\frac{1}{2}})[\{1 + 2K_D/[H^+]^2(2c_M - c_B - [H^+] + K_w/[H^+])\}^{\frac{1}{2}} - 1] \qquad (7)$$

$$[Fe(salen)]^+ + cat^{2-} \overset{K}{\rightleftharpoons} [Fe(salen)(cat)]^- \qquad (8)$$

the calculus 80 experimental points from three different experiments were used. The theoretical curve calculated from this constant fits well the experimental data. Figure 5 shows the distribution diagram for the existing species in solution.

## Discussion

The results of the solution chemistry of $[Fe(salen)]^+$ in dmso–$H_2O$ (80 : 20) are summarized in the Scheme. Acidification of solutions of this compound causes decomposition to give $Fe^{3+}$, salicylaldehyde, and ethylenediammonium cation. The reaction is very slow and completely reversible.[9] On the other hand when $[Fe(salen)]^+$ solutions are basified, $[\{Fe(salen)\}_2O]$ formation occurs.* This reaction presumably

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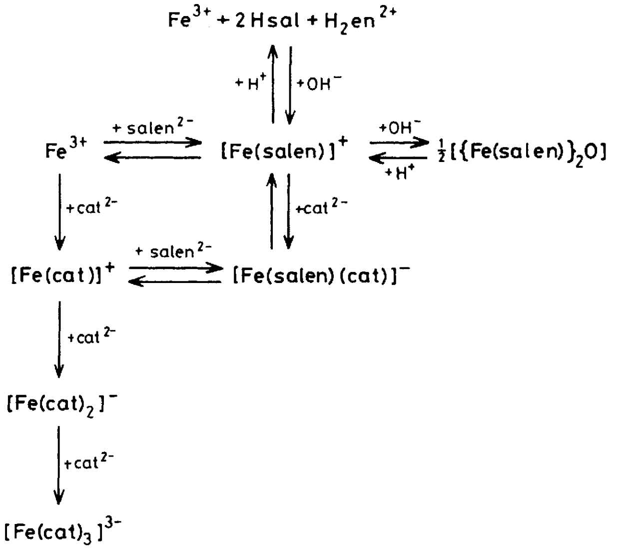
* $[\{Fe(salen)\}_2O]$ decomposed in very basic media to give $salen^{2-}$ and $Fe_2O_3$.



**Scheme.** Hsal = salicylaldehyde, $H_2en^{2+}$ = ethylenediammonium cation

proceeds by deprotonation of one axial $H_2O$ ligand and condensation between two Fe(salen)(OH) units. However, there is no evidence of the existence in equilibrium with $[Fe(salen)]^+$ of other species other than $[\{Fe(salen)\}_2O]$. Thus the solution behaviour of $[Fe(salen)]^+$ is similar to that of iron porphyrins such as $[Fe^{III}(tpp)]$ ($H_2tpp$ = tetraphenylporphyrin) and $[Fe^{III}(tpps)]$ [$H_2tpps^{4-}$ = tetra(*p*-sulphonatophenyl)porphyrin] which easily form μ-oxo-dimers in solution. The reported [11] $K_D$ value for [Fe(tpps)] in aqueous solution is $0.79 \times 10^{-8}$ whereas our value for $[Fe(salen)]^+$ is $5.0 \times 10^{-13}$ mol dm$^{-3}$. Although these values are not strictly comparable, due to differences in solvent and background electrolyte, it is apparent that the tendency to dimerize is greater for the metalloporphyrin.

Although $[\{Fe(salen)\}_2O]$ has been known for some time, a study of its formation in solution from the monomeric species has not been reported previously. This is possibly due to the nature of the solvents previously employed. The complex $[\{Fe(salen)\}_2O]$ is rather soluble in dmso–$H_2O$ (80 : 20) but is less soluble than $[\{Fe(salen)Cl\}_2]$. This fact gives us a very simple and effective procedure to isolate the oxo-complex. Two methods have been reported in the literature for the synthesis of $[\{Fe(salen)\}_2O]$. One was based on the reaction between $H_2salen$ and freshly prepared $Fe_2O_3$,[12] and the other on the oxidation of $[Fe^{II}(salen)]$ by atmospheric $O_2$.[10c] We obtained this compound in crystalline form and in almost quantitative yields by adding, in stoicheiometric amounts, a KOH solution to a solution of $[\{Fe(salen)Cl\}_2]$ using dmso–$H_2O$ (80 : 20) as solvent. In spite of the co-ordinating properties of the solvent, the structure of $[\{Fe(salen)\}_2O]$ in solution must be similar to that of the solid state, with $Fe^{III}$ remaining five-co-ordinate. Thus, the absorption spectra in solution are identical to the reflectance spectrum of the solid.

The acidity constants of catechol in water, dmso, and dmso–$H_2O$ (80 : 20) are shown in Table 1.

The aqueous constants have been reported many times in the literature, and serious difficulties in obtaining a satisfactory $K_{a2}$ value have been found.[13,14] By using dmso–$H_2O$ (80 : 20) as a solvent these difficulties were avoided and a completely reliable $K_{a2}$ value obtained. Catechol acidity increases as the solvent water content is raised. This behaviour is the same as that observed for phenols [15] and other weak acids.[16]

**Table 1.** Acidity constants of $H_2cat$ ($I$ = 0.1 mol dm$^{-3}$, 25 °C)

| Solvent | $K_{a1}$ | $K_{a2}$ | Ref. |
|---|---|---|---|
| $H_2O$ | $6.3 \times 10^{-10}$ | $2.6 \times 10^{-12}$—<br>$2.5 \times 10^{-14}$ | *a* |
| dmso–$H_2O$ (80 : 20) | $1.6 \times 10^{-13}$ | $2.7 \times 10^{-16}$ | This work |
| dmso | $5.4 \times 10^{-16}$ | $1.1 \times 10^{-20}$ | *b* |

[a] Y. Murakami, R. Nakamura, and M. Takanuga, *Bull. Chem. Soc. Jpn.*, 1963, **36**, 669; M. Bartusek and L. Sommer, *J. Inorg. Nucl. Chem.*, 1965, **27**, 2397. [b] F. LLoret, J. Moratal, and J. Faus, *An. Quim.*, 1981, **77B**, 20 2.

The complex $[Fe(salen)]^+$ interacts with catechol in solution giving green solutions. All the experimental data are in agreement with the existence of only one complex of 1 : 1 stoicheiometry in which $cat^{2-}$ acts as bidentate ligand, $[Fe(salen)(cat)]^-$. This compound must be the same as that isolated by Que [2] as a potassium salt. There is no evidence of the existence in solution of protonated species such as [Fe(salen)(Hcat)] [2] or dimeric ones similar to $[Fe_2(salen)_2(tcbd)]$ (tcbd = tetrachlorobenzene-1,2-diol).[7] All these species were isolated under different experimental conditions.

The complex $[Fe(salen)(cat)]^-$ is very stable. Its formation completely inhibits the dimerization of $[Fe(salen)]^+$. Nevertheless the $[\{Fe(salen)\}_2O]$ concentration is not negligible over the whole pH range for which the complex formation takes place and it has a maximum ($\alpha = 0.1$) when the formed complex fraction is $\alpha = 0.45$ (see Figure 5). Thereby, in order to obtain a good stability constant value, it is essential to consider this dimerization equilibrium in the experimental data analysis.

The high equilibrium constant for the $[Fe(salen)(cat)]^-$ formation reaction [equation (8)] indicates that $cat^{2-}$ acts as a bidentate ligand. Unidentate phenolate ligands have a much weaker interaction. *p*-Nitrophenol gives a complex with $K = ca.\ 4 \times 10^2$ which is insufficient to avoid the dimeric oxo-complex formation being the predominant reaction.[17] These results are in opposition with previous reports of Que [2] who suggested a unidentate character for the ligand $cat^{2-}$. However, very recently,[18] the same authors have provided new experimental data supporting chelation of $cat^{2-}$ in $[Fe(salen)(cat)]^-$. The structure of this complex must be similar to that of [Co(salen)(acac)] with $salen^{2-}$ being strongly distorted to allow the binding of a bidentate $cat^{2-}$ (Figure 6). Since the complex forms and dissociates instantaneously it is apparent that the conformational change of the ligand $salen^{2-}$ does not present any significant energetic barrier at room

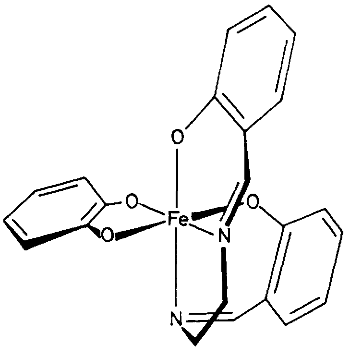


**Figure 6.** Suggested molecular structure for $[Fe(salen)(cat)]^-$

**Table 2.** Overall stability constants in dmso–$H_2O$ (80 : 20) ($I$ = 0.1 mol dm$^{-3}$, 25 °C)

| Compound | log β | Ref. |
|---|---|---|
| $[Fe(salen)]^+$ | 25.85 | 9 |
| $[Fe(salen)(cat)]^-$ | 40.53 | This work |
| $[Fe(cat)]^+$ | 23.90 | * |
| $[Fe(cat)_2]^-$ | 39.90 | * |
| $[Fe(cat)_3]^{3-}$ | 49.65 | * |

* F. LLoret, J. Moratal, and J. Faus, unpublished work.

temperature. Therefore it seems that salen$^{2-}$ displays a remarkable flexibility in solution.

$$[Fe(salen)(solvent)]^+ + cat^{2-} \rightleftharpoons [Fe(salen)(cat)]^- + solvent$$

Fe$^{III}$ probably five-co-ordinate (salen$^{2-}$ ' planar ') Fe$^{III}$ six-co-ordinate (salen$^{2-}$ ' distorted ')

It is interesting to compare the stability constants of $[Fe(salen)]^+$ and $[Fe(salen)(cat)]^-$ with those of iron(III) catecholate complexes in this same solvent (Table 2). The complex $[Fe(salen)]^+$ is almost one hundred times more stable than $[Fe(cat)]^+$ while $[Fe(salen)(cat)]^-$ is only four times more stable than $[Fe(cat)_2]^-$. This relative stability loss can be essentially related to the distortion of salen$^{2-}$. Thus, ' distorted ' salen$^{2-}$ is a poorer ligand than when it has its usual ' planar ' geometry. In the complex this stability loss is largely compensated by the binding of the bidentate ligand.

The complex $[Fe(salen)(cat)]^-$ can be decomposed to give $[Fe(cat)_3]^{3-}$ which is a very stable complex. Fortunately substitution of cat$^{2-}$ for salen$^{2-}$ is only possible in very basic media since the acidity constants of $H_2$salen and $H_2$cat are quite different. As $[Fe(salen)(cat)]^-$ formation is complete in less basic solution this decomposition does not occur.

## Acknowledgements

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