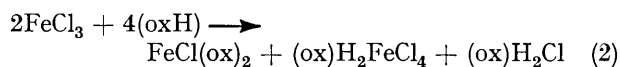
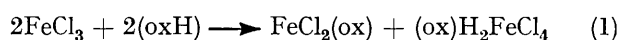


Iron-59 Tracer Study of the Reaction between Iron(III) Chloride and Quinolin-8-ol to give the Chlorobis(quinolin-8-olato)iron(III) Complex

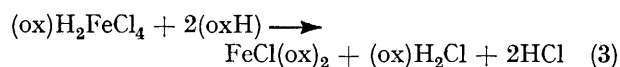
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Tracer studies using ^{59}Fe show that the reaction of quinolin-8-ol and iron(III) chloride to give the chlorobis(quinolin-8-olato)iron(III) complex does not occur by a simple stepwise replacement of chloride ion.

We have previously shown¹ that the complex dichloro-(quinolin-8-olato)iron(III), $\text{FeCl}_2(\text{ox})$ (ox = quinolin-8-olato), is prepared by the reaction of iron(III) chloride (1 mol) and quinolin-8-ol (1 mol) in tetrahydrofuran and that chlorobis(quinolin-8-olato)iron(III), $\text{FeCl}(\text{ox})_2$, is obtained when 2 mol of quinolin-8-ol is used [equations (1) and (2)]. We assumed that in the second reaction



$\text{FeCl}_2(\text{ox})$ is an intermediate which reacts with additional quinolin-8-ol to give the final product. However, the $\text{FeCl}_2(\text{ox})$ complex is insoluble and as the second reaction goes to completion (typical yields are *ca.* 90%), and is relatively fast (the reaction is complete in 15 min) we decided to test our assumption using ^{59}Fe as a tracer. It was necessary to test whether the complex $\text{FeCl}(\text{ox})_2$ came from the reaction of quinolin-8-ol and the other product of the first reaction, tetrachloro(quinolin-8-olium)ferrate(III), because we had also shown¹ that this reaction occurs in diethyl ether-chloroform [equation (3)].



In a typical experiment $\text{FeCl}_2(\text{ox})$ (0.75 mmol), $(\text{ox})\text{H}_2^{59}\text{FeCl}_4$ (0.75 mmol), and (oxH) (1.5 mmol) were stirred in tetrahydrofuran. After 4 h separation gave a precipitate [$\text{FeCl}(\text{ox})_2$ and $(\text{ox})\text{H}_2\text{Cl}$] with 49.4% of the initial activity and a solution [$(\text{ox})\text{H}_2\text{FeCl}_4$] with 50.5% of the initial activity. Equimolar quantities of $\text{FeCl}_2(\text{ox})$ or $\text{FeCl}(\text{ox})_2$ and $(\text{ox})\text{H}_2^{59}\text{FeCl}_4$ in tetrahydrofuran showed less than 5% exchange of iron in 4–5 h.

It is clear that our previous assumption was incorrect and that the complex $\text{FeCl}(\text{ox})_2$ does not come exclusively from the intermediate $\text{FeCl}_2(\text{ox})$. The system iron(III) chloride-quinolin-8-ol must be complex because the results also show that the $\text{FeCl}(\text{ox})_2$ complex does not come exclusively from $(\text{ox})\text{H}_2\text{FeCl}_4$ either. There are a number of competitive reactions (see ref. 1 for further reactions in this system) and the precise distribution of ^{59}Fe must depend upon their relative rates. In this and, probably, related systems, it is therefore not possible to assume that a simple stoichiometry (*e.g.* stepwise replacement of Cl by ox) occurs by a simple sequence.

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¹ M. J. Frazer, A. H. Qureshi, and F. B. Taylor, *J. Chem. Soc. (A)*, 1971, 1712.