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HIGH-SPIN BEHAVIOUR AND CHEMICAL PROPERTIES OF ORGANOMETALLIC DERIVATIVES OF IRON(III)

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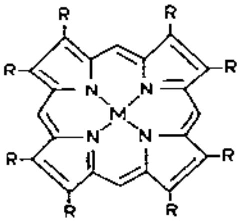
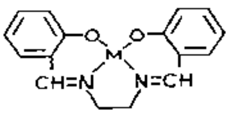
Relatively few examples of organometallic compounds of iron(III) have been reported in the literature. Iron–carbon σ-bonds have been prepared recently[1] by a Grignard reaction on iron(III)-halo derivatives with an etioporphyrin type of structure. The compounds isolated were the *p*-tolyl and the ethyl derivatives as dark blue and purple solids, respectively, sensitive to light. Besides these compounds, no other reports concerning the isolation of iron(III) organometallic compounds have appeared, to the best of our knowledge. The thermal instability of compounds of this type was further suggested by the recently reported[2] failure to isolate iron (III) organometallic compounds, in spite of their suggested formation in the course of the reaction between anhydrous $FeCl_3$ and lithium alkyls. Since the metal–etioporphyrin and the metal-*N,N'*-ethylenebis(salicylideneiminato) skeletons (see structures I and II, respectively) are rather closely related either sterically or electronically, it was considered of interest to see whether it was possible to obtain stable organometallic derivatives of *N,N'*-ethylenebis(salicylideneiminato) iron.



I



II

In this paper a metal complex containing the *N,N'*-ethylenebis(salicylideneiminato) ligand will be abbreviated as [MSaEn], such as [FeSaEn] or [CoSaEn].

In the past years we have reported the occurrence of reductions taking place in non-aqueous solvents with several bis(salicylideneiminato)metal complexes[3–5]. In particular, chemical reductions by sodium metal in tetrahydrofuran were carried out and the corresponding sodium derivatives of formula Na[MSaEn] were isolated in an analytically pure state (M = Fe, Co). It is worth mentioning that we had also previously reported[5] the preparation of the $[CoSaEn]^{2-}$ anion, which was prepared by treating CoSaEn with two

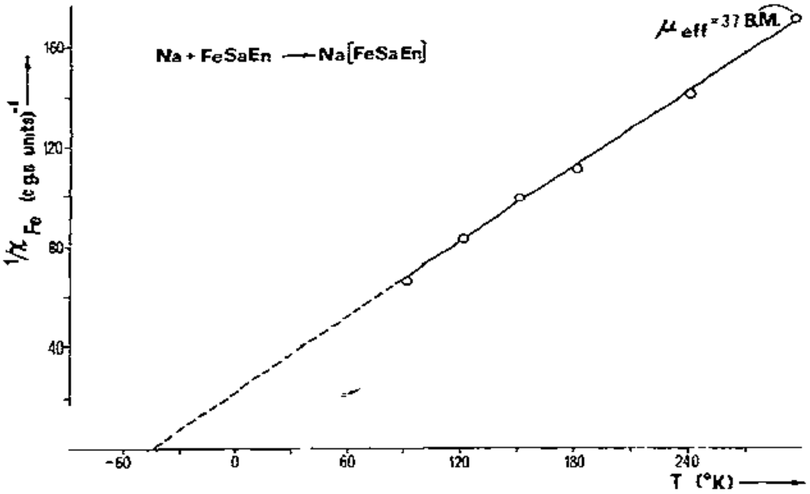


Fig. 1. Temperature dependence of magnetic susceptibility for $[\text{FeSaEn}]^-$

equivalents of sodium metal. We had demonstrated the existence of the anion by the reaction

$$[\text{CoSaEn}]^{2-} + \text{CoSaEn} \rightarrow 2\ [\text{CoSaEn}]^- \qquad (1)$$

Recently, Russian workers[6] have confirmed the existence of the anion by electron transfer reactions to cyclooctatetraene to give $C_8H_8{}^{2-}$ and $[\text{CoSaEn}]^-$.

The most interesting properties of these compounds are (*a*) the bulk magnetic susceptibilities, and (*b*) the chemical reactivity, especially toward electrophilic reagents such as alkyl halides. As far as magnetic susceptibility measurements are concerned, the $[\text{FeSaEn}]^-$ and the $[\text{CoSaEn}]^-$ anions can be regarded as d^7 and d^8 systems of, respectively, high-spin and low-spin behaviour. We have, in fact, established that our previous results[5] on the magnetic properties of Na[CoSaEn], suggesting the presence of a residual small paramagnetism, were in error because of partial oxidation of the samples. Under the best operative conditions, the sodium derivative of cobalt is diamagnetic.

The reduction of FeSaEn takes place in tetrahydrofuran as solvent by using the stoicheiometric amount of sodium

$$\text{FeSaEn} + \text{Na} \xrightarrow{\text{THF}} \text{Na}\ [\text{FeSaEn}] \qquad (2)$$

The sodium derivative is then precipitated from the resulting green solution by partial evaporation of the solvent and addition of heptane. The deep blue solid is extremely sensitive to air and has to be handled with air strictly excluded. The magnetic susceptibility of this compound was measured by the Gouy method and found to follow the Curie–Weiss law reasonably well from room temperature down to liquid nitrogen temperature (Fig. 1). The value of the magnetic moment at room temperature is 3.71 BM, quite close to the theoretical spin-only value (3.87 BM) for three unpaired electrons. The Weiss con-

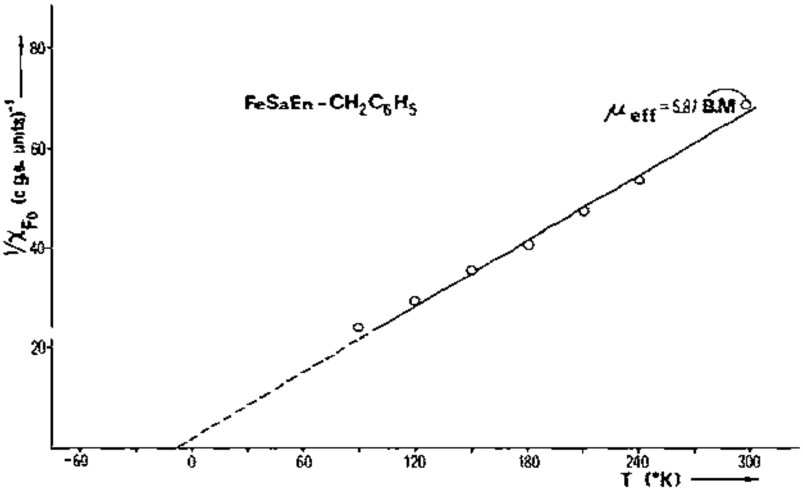


Fig. 2 Temperature dependence of magnetic susceptibility for FeSaEn–$CH_2C_6H_5$

stant is –45°

It has previously been observed[4,5,7] that $[CoSaEn]^-$ reacts with organic halides to give the corresponding cobalt(III) organometallic compounds

$$[CoSaEn]^- + R{-}X \rightarrow CoSaEn{-}R + X^- \qquad (3)$$

In view of the presently reported magnetic properties of $[CoSaEn]^-$, reaction (3) can be rationalised in terms of an oxidative addition to a planar d^8 system such as those usually encountered with cobalt(I), rhodium(I) and iridium(I)[8,9] Reaction (3) can, in fact, be interpreted as the intermediate formation of an anionic cobalt(III) organometallic derivative, $[CoSaEn(R)X]^-$ The latter would then be unstable with respect to X^- elimination and formation of the neutral cobalt(III) organometallic compound. Consistent with this view is the fact under the initial conditions of reaction (3), i.e. addition of the alkyl halide to the solution of $[CoSaEn]^-$ at ca. –80° C, no precipitation of sodium chloride was observed, in spite of the fact that the change of colour from green to orange takes place practically within the time of mixing Sodium chloride elimination usually takes place at room temperature and is completed by addition of water in the case of the cobalt complexes[5]

In view of past experience with cobalt complexes, a reaction similar to (3) was also carried out with $[FeSaEn]^-$

$$[FeSaEn]^- + C_6H_5CH_2Cl \rightarrow Cl^- + FeSaEn{-}CH_2C_6H_5 \qquad (3)$$

Reaction (4) was carried out under conditions similar to those previously reported for the cobalt complex After addition of water, the benzyl derivative was isolated as red needle-like crystals in about 90% yield Recrystallisation of the iron(III) organometallic compound was carried out by dissolution in tetrahydrofuran and precipitation with heptane

The compound is very sensitive to air oxidation (see below) and is light-sensitive, as expected for a compound containing metal carbon σ-bonds

Besides the benzyl derivative, the phenyl derivative, FeSaEn$-C_6H_5$ was also prepared and characterised*, by reaction of the phenyl Grignard reagent with FeSaEn$-$I in tetrahydrofuran as solvent

$$\mathrm{FeSaEn{-}I} + \mathrm{C_6H_5MgBr} \rightarrow \mathrm{FeSaEn{-}C_6H_5} + \mathrm{MgBrI} \qquad (5)$$

The phenyl compound was isolated from the reaction mixture by a procedure similar to that previously mentioned for the benzyl derivative

Both the phenyl and the benzyl derivatives of iron (III) are thermally unstable and reactive towards oxygen The results obtained from the investigation of the behaviour of the organometallic derivatives towards heat and oxygen represent an additional piece of evidence for the presence of iron—carbon bonds in these compounds The reactions

$$2\ \mathrm{FeSaEn{-}R} \rightarrow 2\ \mathrm{FeSaEn} + \mathrm{R{-}R} \qquad (6)$$

$$2\ \mathrm{FeSaEn{-}R} + \tfrac{1}{2}\,\mathrm{O_2} \rightarrow [\mathrm{FeSaEn}]_2\mathrm{O} + \mathrm{R{-}R} \qquad (7)$$

have been established. Although the reaction of the benzyl derivative with oxygen was somewhat more complicated, with the phenyl derivative the dimeric μ-oxo-bis [ethylenebis(salicylideneiminato)iron(III)] [10] was the only isolable compound We have never obtained substantial evidence for the formation of peroxo-alkyl compounds of the type found [11,12] in certain alkyl-cobaloximes. We believe that in reaction (7) the determining factor is the labilisation of the metal—carbon bond, prior to attack by oxygen.

Both reactions (6) and (7) are typical of metal—carbon bonds and they therefore exclude the possibility that the alkyl group might be attached to some other point of the molecule Further evidence of iron—carbon bonds in these compounds came from the magnetic susceptibility data, the FeSaEn—R compounds are thermally much less stable than, for example, the corresponding low-spin CoSaEn—R derivatives[4,5,15]. However, a satisfactory Curie—Weiss plot was obtained (see Fig 2), the Weiss constant was found to be about $-9°$ and the magnetic moment at room temperature was 5 87 BM, very close to the theoretical value (5 92 BM) for five unpaired electrons Details concerning the magnetic susceptibility measurements have been published elsewhere[13]

The high-spin behaviour of FeSaEn$-CH_2C_6H_5$ is very unusual in organometallic chemistry Only the σ-mesityl and the σ-naphthyl derivatives of chromium(II)[14] recently prepared by Stolze and Hahle behave similarly. The iron(III) organometallics with the etioporphyrin type of structure[1] might also be high-spin systems but unfortunately no detailed magnetic susceptibility data were reported to establish this point

In accordance with the occupancy of the highest molecular orbitals, as suggested by magnetic susceptibility data, the FeSaEn—R compounds are thermally much less stable than for example, the corresponding low-spin CoSaEn—R derivatives[4,5,15] However,

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* Unless otherwise stated, all the new compounds reported in this paper analysed correctly for the formulations given

the iron(III) compounds were isolated by normal operating procedures at room temperature and should be regarded as stable at least in the solid state, provided air and light are excluded.

We have also attempted the preparation of the corresponding methyl and acetyl derivatives In both cases reactions between the [FeSaEn]$^-$ anion and the proper organic halide were observed but no analytically pure product could be obtained

By analogy with the magnetic results obtained[16] for the chloro derivatives FeSaEn–Cl and [FeSaEn–Cl]$_2$, the magnetic susceptibility data of the present work might be interpreted in terms of a mononuclear pentacoordinate structure for the benzyl derivative, FeSaEn–$CH_2C_6H_5$ This is indicated by the value of the magnetic moment at room temperature and by the relatively small value of the Weiss constant, suggesting that no important interactions take place between different iron centres, as one would expect for a dimeric, oxygen-bridged structure Of course, the results of an X-ray investigation would be required to confirm this suggestion

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