

Figure 2. ^1H NMR spectra (in toluene- d_8) in the hydride region of $\text{IrH}_3(\text{CO})[(4\text{-ClC}_6\text{H}_4)_3\text{P}]_2$: (a) at room temperature; (b) after passage of a stream of N_2 through the solution for 2 h; (c) after cooling of the solution to -20°C .

10) is increased by purging the solution with N_2 . Although the bridged intermediate 10 (or something very similar to it) is the only one whose existence is evident by NMR, others, whose exchange rate at room temperature is relatively slow, may also be present and contribute to isomerization-isotomerization reactions.

Finally, we come to the question of the apparent trans addition of H_2 (D_2) to 6 reported previously.¹ It is clear from the reaction of the styrene complex with D_2 that no products arising from trans addition are produced at -30°C . When the solution containing 2 and 3 is warmed to room temperature, the isotopomers 4 and 9 appear. Since the appearance of 4 parallels that of 9, both in terms of rate and in terms of the subsequent appearance of dihydrides, it is reasonable to assume that 4 is produced by the same mechanism proposed above the production of 9.

Experimental Section

The trihydrides 7 and 7' were prepared by following a variation of a previously described procedure.² Reagent grade styrene was freshly distilled under reduced pressure of N_2 from CaH_2 immediately prior to the preparation of the styrene complex.

All NMR measurements were made on solutions in CD_2Cl_2 (99.8% minimum purity, Merck Sharp and Dohme, Canada, Ltd.) as solvent (unless specified). Spectra were recorded on a Varian XL-200 spectrometer at 200.057 MHz. All reported chemical shifts are relative to an internal $(\text{CH}_3)_4\text{Si}$ standard.

Synthesis of Hydridocarbonylbis(triphenylphosphine)(η^2 -styrene)-iridium(I). Freshly distilled styrene (20 mL) was added under nitrogen to $\text{IrH}_3(\text{CO})(\text{PPh}_2)_2$ (0.35 g). The solution was stirred at 45°C for 20 min with a constant stream of nitrogen passing through, and then the styrene solvent was rapidly stripped off under vacuum to yield

a pale yellow solid. The crude product was contaminated with small amounts of the tris(phosphine) complex 1 and an unidentified hydride (^1H NMR: $\delta -15.4$ (t)). The crude product was recrystallized from styrene/heptane at -20°C . NMR (CD_2Cl_2 , -30°C): $\delta -11.52$ (d) and -11.67 (d) (hydride resonance of less abundant isomer, $J_{\text{HP}} = 16.5$ Hz); $\delta -12.03$ (pseudotriplet, hydride resonance of more abundant isomer, $J_{\text{HP}} \approx 19.0$ Hz); $\delta 2.3, 2.4, 2.6, 2.8, 3.8$ (broad multiplets due to coordinated styrene). IR (Nujol mull): $\nu_{\text{CO}} = 1939\text{ cm}^{-1}$; $\nu_{\text{IrH}} = 2059\text{ cm}^{-1}$.

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Contribution from the Divisione Chimica, ENEA, Casaccia, Rome, Italy, and Istituto Chimica Fisica e Industriale, Università di Cagliari, Cagliari, Italy

On the Structure of Iron(III) Chloride Solutions

G. Giubileo, M. Magini,* G. Licheri, G. Paschina, G. Piccaluga, and G. Pinna

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The structure of iron(III) chloride solutions has been widely investigated by X-ray diffraction methods. The literature, up to 1979, has been cited in a recent work in which iron(III) chloride solutions, from 2 to 6 M, have been examined.¹ The main conclusion reached in that work was that extensive complex formation does occur in all solutions and that octahedral $\text{Fe}(\text{H}_2\text{O})_{6-n}\text{Cl}_n^{3-n}$ ($n = 1-3$) or tetrahedral FeCl_4^- complexes are the prevailing species at the different concentrations examined. A quantitative evaluation of the complex formation, expressed by the average number of Cl^- ions bonded per Fe^{3+} ion, n_{Cl} , was also made.

Since 1979, further papers have been published on this matter. In one of them, the structure of the undercooled hydrated $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ melt was examined at room temperature.² Evidence of polynuclear complex formation, probably related to the presence of the bitetrahedral Fe_2Cl_6 molecule, was obtained. In two other papers, published by Wertz and his co-workers,^{3,4} solutions, of concentrations approximately the same as ours,¹ were examined. The conclusions there reported, however, are dramatically different from ours. The new points claimed by Wertz and coworkers are as follows:

(a) Two solutions prepared from the hydrated $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ salt (3.7 and 4.1 M), and examined by X-ray diffraction 1 week after their preparation, *do not show any complex formation*.³ The solute species was identified as $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. The first peak of the radial curve of the two solutions occurs at 2.03/2.04 Å, which is just the sum of the Fe^{3+} (0.64 Å) and H_2O (1.40 Å) ionic radii. We have previously obtained,¹ for a 4.2 M solution also prepared with the hydrated salt, an n_{Cl} value of 3.

(b) The 3.7 M solution was reexamined after 14 months, and then an average solute species, approximately $\text{FeCl}_{1.5}(\text{H}_2\text{O})_{4.5}^{1.5+}$, was claimed to occur.⁴ The first peak of the distribution curve is centered at 2.16 Å, which is a weighted average of $\text{Fe}-\text{OH}_2$ (2 Å) and $\text{Fe}-\text{Cl}$ (~ 2.3 Å) interactions. In our previous work¹ we did not check the effect of time on the structure of the solutions. Usually our solutions, unless otherwise needed, are examined soon after their preparation so that our previous results are to be considered as obtained from freshly prepared solutions.

* To whom correspondence should be addressed at the ENEA.

Table I. Composition of the Solutions, Experimental Conditions, and Characteristics of the First Peak in the Radial Curves

soln	[Fe ³⁺], M	conditions			1st max	
		time	starting salt	diffractometer	position <i>r</i> _{max} , Å	10 ⁻³ <i>D</i> (<i>r</i> _{max}), e ² Å ⁻¹
H _R ^o	3.68	<i>t</i> = 0	FeCl ₃ ·6H ₂ O	Rome	2.25	10.72
H _R '	3.68	<i>t</i> = 8 months	FeCl ₃ ·6H ₂ O	Rome	2.25	11.33
H _C ^o	3.61	<i>t</i> = 0	FeCl ₃ ·6H ₂ O	Cagliari	2.25	11.90
A _R ^o	3.65	<i>t</i> = 0	FeCl ₃	Rome	2.25	10.97

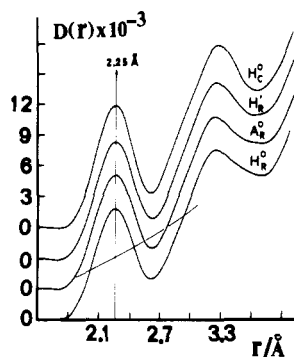


Figure 1. Radial distribution functions, $D(r)$ ($e^2 \text{ \AA}^{-1}$), for the four solutions examined (solid strong lines) and the $4\pi r^2 \rho_0$ function¹ drawn on the H_R^o curve (weak solid line). The meaning of the labels in each curve is given in the text and in Table I.

(c) Two solutions freshly prepared from the anhydrous salt (4.1 and 4.8 M), and examined by X-ray diffraction, definitely show complex formation between Fe³⁺ and Cl⁻ ions.³ The first peak of the radial curves is centered at 2.28 and 2.27 Å and the n_{Cl} values are 3.5 and 4 for the 4.1 and 4.8 M solutions, respectively. The coordination suggested for the Fe³⁺ ion is tetrahedral.

Although we had no information on the effect of aging time and solution preparation with the hydrated or anhydrous salt, the results described in Wertz's papers seemed to us in strong contradiction with our previous results and with general information given in the literature about iron(III) chloride solutions.

First of all the references examined in the previous paper,¹ which include works on solutions examined by different techniques and in various chemical states, never mentioned an aging effect unless the very slow hydrolysis equilibria⁵ were purposely promoted. Hydrolysis, of course, does also occur, to a limited extent,⁶ in concentrated "neutral" solutions (i.e., solutions prepared from a stoichiometric salt dissolved in water). This phenomenon, however, is not, in our experience, time dependent.

Secondly, we were surprised that, starting from hydrated or from anhydrous iron salt, states completely different were obtained for solutions of the same concentration. This would

mean that solutions really far from the equilibrium state were to be supposed.

The third consideration that moved us to consider the question further was that the presence in the literature of so different results obtained for so similar solutions by the same technique is puzzling.

We have therefore reexamined by X-ray the following 3.7 M solutions (the same concentration as one of Wertz's solutions): (1) neutral solution, prepared from FeCl₃·6H₂O, examined as soon as prepared in the Rome diffractometer (H_R^o); (2) solution as above, independently prepared and run in the Cagliari diffractometer (H_C^o); (3) H_R^o reanalyzed after 8 months (H_R'); (4) neutral solution, prepared from the anhydrous FeCl₃ salt, examined as soon as prepared in the Rome diffractometer (A_R^o).

The four collected sets of data have been all treated in exactly the same way as we have done before.¹ The four resulting radial distribution curves are shown in Figure 1. Table I gives the chemical compositions of the four solutions together with data related to the first peak of their radial curves. The coincidence in both the positions of the first maximum and the general shape of the four curves is very good. The greatest, still very little, difference is between H_R^o and H_C^o (freshly prepared solutions of the same concentration run in two different diffractometers). The H_C^o first peak is higher but also sharper than that of H_R^o so that the whole included areas are nearly the same under both peaks. The maximum is, in any case, always *exactly* centered at 2.25 Å in the four curves showing that, as we had thought, we have true equilibrium solutions: the same species must then be present in all cases. The four curves, finally, are very similar to that of the previously examined 4.2 M solution¹ (whose peak was centered at 2.27 Å), showing that the same complex formation, approximately, is occurring in the present solutions.

The present results unambiguously indicate that (a) complex formation *does occur* in a solution freshly prepared from FeCl₃·6H₂O, (b) no aging effect occurs in such a solution, and (c) solutions prepared from either the hydrated or anhydrous iron(III) chloride salt *do give* the same radial distribution curves.

The actual results, therefore, contradict Wertz's results.^{3,4} We have found two sources, both experimental, that can explain such large discrepancies. First the densities of Wertz's solutions³ do not vary linearly with iron(III) concentration—whatever the starting salt—as they should. Second, the experimental scattering data themselves seem very different as can be seen by comparing Figures 1 of ref 1 and 3. This second point is, in our opinion, the main cause of the differences discussed above.

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