CONTRIBUTION FROM THE W. A. NOYES LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Iron(III)–Chloro Complexes in the Solvent N,N-Dimethylacetamide

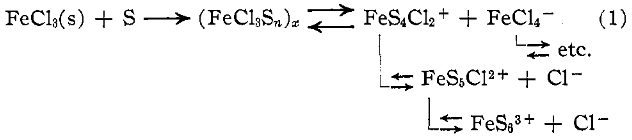
BY RUSSELL S. DRAGO, ROBERT L. CARLSON,[1] AND KEITH F. PURCELL

Received July 20, 1964

The chloro complexes of iron(III) which exist in the solvent N,N-dimethylacetamide have been examined in dilute solution over the mole ratio range 0 to 14 moles of chloride per mole of iron(III). Evidence for the existence of mono-, di-, and tetrachloro complexes is presented. When iron(III) chloride is dissolved in this solvent, the principal species formed are $Fe(DMA)_mCl_2^+$ and $FeCl_4^-$.

Introduction

In a previous article,[2] a coordination model was presented as an alternative to the solvent system concept for explaining the behavior of solutes in certain nonaqueous solvents. According to this model, the equilibria describing the reactions which occur when the acidic solute iron(III) chloride is dissolved in a donor solvent are formulated as



$$\begin{aligned} FeCl_3(s) + S \longrightarrow (FeCl_3S_n)_x &\rightleftharpoons FeS_4Cl_2^+ + FeCl_4^- \quad (1)\\ &\qquad\qquad\qquad \rightleftharpoons \text{etc.}\\ &\leftrightarrows FeS_5Cl^{2+} + Cl^-\\ &\qquad \leftrightarrows FeS_6^{3+} + Cl^- \end{aligned}$$

where S is a donor solvent molecule. Very little is known about the composition or structure of the addition compounds $(FeCl_3S_n)_x$ that exist in some of these systems.[3] Often the number of solvent molecules coordinated to a cation in solution is not known but is guessed at from the composition of solids which are isolable from that solution.

It was proposed under this model that the positions of the above equilibria are a function of the solvent donor strength and the ability of the solvent to solvate the various species. The focusing of attention on these essential solvent properties is one of the principal features of the coordination model. With this in mind, it can be seen that further advances in our understanding of nonaqueous solvent behavior will depend upon whatever information we may glean about the species present when a solute is dissolved in various nonaqueous solvents. In this article we report a thorough investigation of the chloro complexes which arise when iron(III) chloride is dissolved in N,N-dimethylacetamide. The complex species of this system were established by ultraviolet spectroscopy. The spectra of the various chloro species were established by studying the spectrum of solutions containing varying ratios of LiCl (or $(C_2H_5)_4NCl$) and $Fe[CH_3C(O)N(CH_3)_2]_6(ClO_4)_3$. Over the region of 2 Cl^- to 4 Cl^- per iron(III), the equilibrium between Fe^{3+}, $CH_3C(O)N(CH_3)_2$, and Cl^- in dilute solution can be formulated as

$$Fe(DMA)_mCl_2^+ + 2Cl^- \rightleftharpoons FeCl_4^- + mDMA \qquad (2)$$

where DMA is the abbreviation for N,N-dimethylacetamide. It is estimated that the total concentration of all other iron species at chloride to iron(III) ratios between 2 and 4 (*e.g.*, $FeCl_3 \cdot DMA$) does not exceed 10% of the total iron present. Consequently, when small amounts ($\sim 10^{-3}$ to 10^{-4} *M*) of iron(III) chloride are dissolved in DMA, the principal iron species formed are $Fe(DMA)_mCl_2^+$ and $FeCl_4^-$.

Experimental

Apparatus.—Ultraviolet absorption spectra were obtained on a Beckman Model DU quartz spectrophotometer. The optical densities were measured in matched 1.0-cm. quartz cells against the solvent as a reference. Infrared studies were carried out using a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics.

Reagents and Solvents.—N,N-Dimethylacetamide was shaken over barium oxide and distilled under reduced pressure from fresh barium oxide. The middle fraction was collected and redistilled under reduced pressure in the presence of calcium hydride.

Anhydrous iron(III) chloride (Matheson Coleman and Bell) was resublimed under a stream of dry nitrogen and stored in a desiccator over phosphorus pentoxide.

All solutions were prepared and the glass-stoppered quartz spectrophotometer cells were filled inside a drybox.

Tetramethylammonium tetrachloroferrate(III) was prepared by dissolving iron(III) chloride in a benzene–ethanol mixture and adding a stoichiometric amount of tetramethylammonium chloride. Evaporation of the solvent and cooling yielded yellow-green crystals which were filtered off in a drybox and dried in a vacuum desiccator over phosphorus pentoxide.

Anal. Calcd. for $C_4H_{12}NFeCl_4$: C, 17.67; H, 4.45; N, 5.15. Found: C, 17.68; H, 4.42; N, 5.07.

Preparation of Hexakis(N,N-dimethylacetamide)iron(III) Perchlorate.—To 2.90 g. (0.014 mole) of anhydrous silver perchlorate dissolved in 30 ml. of N,N-dimethylacetamide was added 0.75 g. (0.0046 mole) of anhydrous iron(III) chloride dissolved in 20 ml. of N,N-dimethylacetamide. After standing for 12 hr. to ensure complete precipitation of the silver chloride, the solid was filtered off and approximately 300 ml. of dry ether was added to the filtrate. A yellow precipitate was obtained which was filtered, washed with ether, and dried under vacuum over phosphorus pentoxide. The entire operation was carried out in a drybox.

Anal. Calcd. for $C_{24}H_{54}N_6O_{18}Cl_3Fe$: C, 32.87; H, 6.21; N, 9.58; Fe, 6.37. Found: C, 32.72; H, 6.29; N, 9.42; Fe, 6.31.

Attempted Preparation of $Fe(DMA)_4Cl_2ClO_4$.—Attempts were made to prepare this complex from iron(III) chloride solutions in DMA to which enough $AgClO_4$ or $Fe(DMA)_6(ClO_4)_2$ was added to give a chloride to iron(III) mole ratio of 2:1. Flooding this solution with ether produced an oil from which a solid separated on standing. Elemental analysis indicates the desired compound

---

[1] Abstracted in part from the Ph.D. thesis of Robert L. Carlson, University of Illinois, 1962.

[2] D. W. Meek and R. S. Drago, *J. Am. Chem. Soc.*, **83**, 4322 (1961).

[3] V. Gutman and M. Baaz, *Monatsh. Chem.*, **90**, 729 (1959).

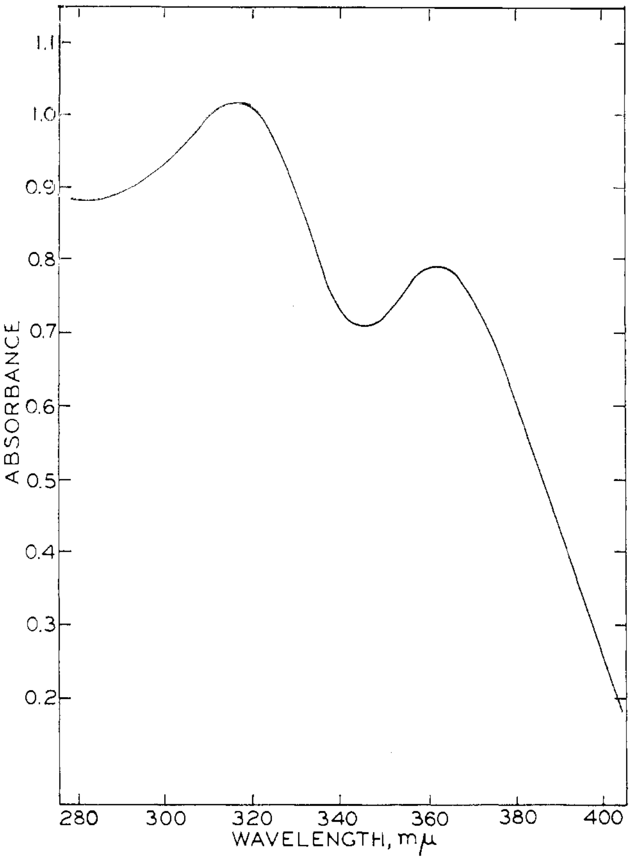


Figure 1.—Ultraviolet spectrum of iron(III) chloride (1.6×10^{-4} *M*) in DMA.

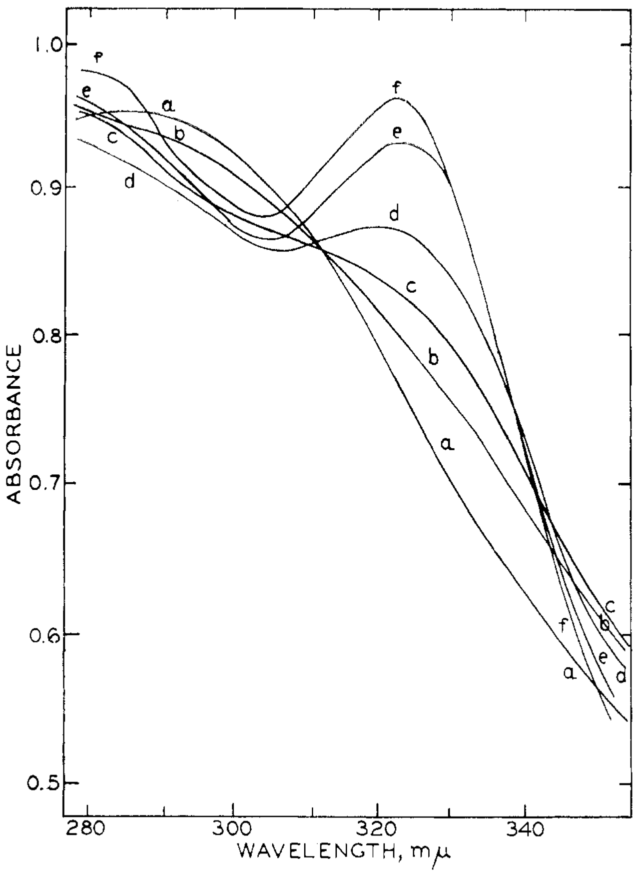


Figure 2.—Ultraviolet spectra of the system $Fe(DMA)_6(ClO_4)_3$–LiCl (iron(III) concentration is 1.3×10^{-4} *M*): a, $Fe(DMA)_6(ClO_4)_3$; mole ratios of LiCl to $Fe(DMA)_6(ClO_4)_3$ in b, 0.3:1; in c, 0.6:1; in d, 0.9:1; in e, 1.2:1; in f, 1.8:1.

was not obtained. It could not be obtained by recrystallization of the solid that was isolated.

Results

The spectrum of iron(III) chloride in the solvent DMA is represented in Figure 1. In Figure 2, the spectra obtained for a DMA solution 1.95×10^{-4} *M* in $Fe(DMA)_6(ClO_4)_3$ and for solutions of this iron concentration with added LiCl are presented. The mole ratios of Cl^- to iron(III) range from 0 to 1.8. In Figure 3, spectra for the same system are shown over the mole ratio range of 2.1 to 4.1 chloride ions per iron(III). The spectrum in Figure 3 labeled d is identical with the spectrum obtained when $(CH_3)_4NFeCl_4$ is dissolved in this solvent.[4] The spectrum obtained at a mole ratio of 3 Cl^- to iron(III) is identical with that obtained when the same solution concentration of iron(III) is achieved by dissolving $FeCl_3$ in DMA. This same spectrum can also be obtained by adding enough $AgClO_4$ to a solution of $(CH_3)_4NFeCl_4$ to precipitate one-fourth of the chloride ion. These experiments demonstrate that equilibrium has been attained in these systems.

Discussion

The infrared spectrum of a CH_2Cl_2 solution of $Fe(DMA)_6(ClO_4)_3$ indicates that oxygen coordination occurs. The carbonyl stretching vibration occurs at a lower frequency in this complex than in the uncomplexed ligand. Unfortunately, there are no bands in the infrared spectrum of the free ligand that are not masked by complexed ligand bands. As a result the number of coordinated amide molecules in solution could not be determined for $Fe(DMA)_6^{3+}$ and the chloro species $Fe(DMA)_nCl^{2+}$ and $Fe(DMA)_mCl_2^+$. Attempts at the preparation of $Fe(DMA)_5Cl^{2+}$ and $Fe(DMA)_4Cl_2^+$ also failed. Consequently, we are speculating about the number of DMA molecules included in our formulas of the monochloro and dichloro iron(III) species. The coordination number six will be assumed here for all cationic iron(III) species, for this coordination number is most common for cationic iron(III) complexes. The existence of monochloro and dichloro species over the range of Cl^-/Fe^{III} ratios up to 2.1 is rigorously confirmed by an analysis of the spectral data. Curve a of Figure 1 corresponds to the species obtained when $Fe(DMA)_6(ClO_4)_3$ is dissolved in DMA. As chloride ion is added to produce mole ratios of 0.3, 0.6, and 0.9 LiCl to iron(III) (curves b, c, and d, respectively), the intensity of absorption decreases at 290 mμ and increases at 330 mμ. However, at 350 mμ, the intensity increases for mole ratios of 0.3 and then 0.6 and then decreases for a mole ratio of 0.9 (curve d). Three species are required to explain this behavior and these are most certainly $Fe(DMA)_6^{+3}$, $Fe(DMA)_5Cl^{+2}$, and $Fe(DMA)_4Cl_2^+$.

---

[4] It has been reported that LiCl is completely dissociated in DMA at 25° up to concentrations of 0.02 *M*: G. R. Lester, J. W. Vaughn, and P. G. Sears, *Trans. Kentucky Acad. Sci.*, **19**, 28 (1958).

Support for this conclusion will be presented as the discussion proceeds. The stepwise equilibrium constant for the formation of the monochloro iron complex must be smaller than that for the dichloro complex because appreciable quantities of the dichloro species are formed at a mole ratio of 0.9 LiCl per iron(III). Over the mole ratio range 0.9 to 1.8 LiCl per iron(III), all of the iron in the system is converted to $Fe(DMA)_4Cl_2^+$ and the spectrum represented by curve f is essentially that of this species. The lack of formation of $FeCl_4^-$ at 2:1 Cl^- to iron(III) is indicated by the absence of an absorption maximum near 360 mμ (*vide infra*).

The curves in Figure 3 are characterized by the existence of two isosbestic points at about 390 and 345 mμ. This is an indication that only two iron species exist in DMA solution in the mole ratio region of 2.1 to 4.1 LiCl to iron(III). Spectrum d of Figure 3 is identical with the spectrum obtained when $(CH_3)_4NFeCl_4$ is dissolved in DMA and, furthermore, this absorption curve is essentially unchanged with the addition of a tenfold excess of lithium chloride (*i.e.*, a Cl^- to iron(III) mole ratio of 14). The change in absorbance on going from 4 Cl^- to 14 Cl^- per iron(III) is less than 3%. This spectrum is also very similar to that obtained for $FeCl_4^-$ in a wide variety of solvents (triethyl phosphate,[2] aqueous HCl,[5] $(C_2H_5)_2O$,[6] C_2H_5Br,[6] dioxane,[6] $POCl_3$,[7] and $C_6H_5POCl_2$[7]). This substantiates the assignment of this spectrum as due to the species $FeCl_4^-$ and suggests the representation of the equilibrium which occurs over this chloride to iron(III) mole ratio range by the equation

$$Fe(DMA)_4Cl_2^+ + 2Cl^- \rightleftarrows FeCl_4^- + 4DMA \qquad (3)$$

The similarity in the spectra of $FeCl_4^-$ in these different solvents is an indication that there is no solvent coordination and this is a tetrahedral iron(III) species. Within experimental error, Beer's law is obeyed for DMA solutions of tetramethylammonium tetrachloroferrate over the concentration range 0.75×10^{-4} to 1.91×10^{-4} *M*.

Unless the molar absorptivity of the trichloro iron(III) species has the same molar absorptivity as $FeCl_4^-$ and the dichloro iron species at both isosbestic points, we can conclude that there must be only a very small amount of trichloro species present.

The molar absorptivities of $Fe(DMA)_4Cl_2^+$ and $FeCl_4^-$ reported in Table I were determined from the spectra of solutions containing varying concentrations of $Fe(DMA)_6(ClO_4)_3$ with mole ratios of 2:1 and 4:1 chloride ion to iron(III).

Since in a solution 2×10^{-4} *M* in iron(III) with a mole ratio of four chlorides per iron(III) nearly all of the iron is in the form of $FeCl_4^-$, we can set a lower limit of 10^{10} on the equilibrium constant for the reaction $Fe(DMA)_4Cl_2^+ + 2Cl^- \rightleftarrows FeCl_4^- + 4DMA$. In view of the anticipated nonideality of this system with respect to ion pairing, we did not undertake a more complete study of the equilibrium constant.

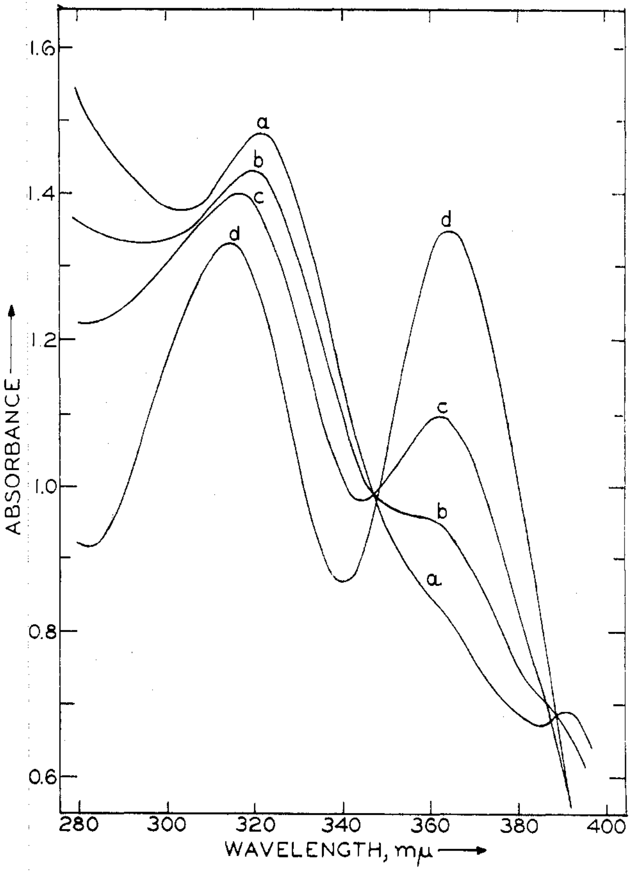


Figure 3.—Ultraviolet spectra of the system $Fe(DMA)_6(ClO_4)_3$–LiCl (iron(III) is 2.2×10^{-4} *M*): mole ratios of LiCl to $Fe(DMA)_6(ClO_4)_3$ in a, 2.1:1; in b, 2.6:1; in c, 3.1:1; in d, 4.1:1.

TABLE I

MOLAR ABSORPTIVITIES (L. CM.$^{-1}$ MOLE^{-1}) OF $Fe(DMA)_4Cl_2^+$ AND $FeCl_4^-$ IN $CH_3C(O)N(CH_3)$

λ, mμ	ε $Fe(DMA)_4Cl_2^+$	ε $FeCl_4^-$
290	7400 ± 70	4920 ± 70
330	7120 ± 50	5420 ± 100
340	5840 ± 50	4420 ± 20
355	4430 ± 80	6195 ± 45
380	3340 ± 140	5170 ± 70

This study enables us to conclude that when iron(III) chloride is dissolved in DMA the principal species present in dilute solution are $Fe(DMA)_4Cl_2^+$ and $FeCl_4^-$.

Acknowledgment.—The authors wish to thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT(11-1)758.

---

(5) G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, 1435 (1953).

(6) H. L. Friedman, *J. Am. Chem. Soc.*, **74**, 5 (1952).

(7) M. Baaz, V. Gutman, and L. Hubner, *Monatsh. Chem.*, **91**, 537 (1960).