An Electron Paramagnetic Resonance Study of Mn(II)-Chloro Complex Formation in N,N-Dimethylformamide

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EPR spectra differing in hyperfine splitting have been reported for Mn(II) ions in N,N-Dimethylformamide (DMF) when using Mn(ClO₄)₂ and MnCl₂. The difference in the reported spectra is shown to be due to the species MnCl₂⁺ by a mole ratio plot. The presence of MnCl₂⁺ is also indicated by a mole ratio plot. Three basic spectra, differing in hyperfine splitting, are obtained for solutions of Mn(ClO₄)₂ in DMF to which varying amounts of chloride ion have been added. \( \Delta H^0 \) for the equilibrium reaction of the species MnCl₂⁺ and MnCl₂⁺ was determined from the variation of the formation constant, \( K_f \), with temperature over the range 25°C to 116°C. Values for \( \Delta F^0 \) and \( \Delta S^0 \) at 25°C are also given.

Mn(II)-chloro complexes have been studied previously in aqueous solutions by spectrophotometric, ¹, anion exchange ², cation exchange ³, refractometric ⁴, polarographic ⁵, and EPR ⁶ methods, in water-alcohol mixed solvents by EPR and ion-exchange ⁷, and in acetonitrile, propanediol-2,2-carbonate and trimethylphosphate by spectrophotoelectric, potentiometric, and conductometric ⁸ methods. The use of EPR spectroscopy to study ionic complexes in solution has not been so widely used as other forms of absorption spectroscopy, but is a useful technique for the study of complex formation involving transition metal ions since EPR spectra are obtainable only for substances containing unpaired electrons. Few studies of this nature in nonaqueous solvents have been reported, although Swanson and Laurie ⁹ have investigated Iron(III)-chloro complexes by EPR in a number of organic solvents including N,N-Dimethylformamide (DMF). Chan, Fung, and Lutje ¹⁰ have investigated Mn(II) complexes including chloro complexes in acetonitrile while Levanon and Luz ¹¹ have studied these complexes in methanol.

The EPR spectrum of Mn(II) ions in several nonaqueous solvents including DMF has been the subject of two recent publications ¹², ¹³. In their study of the electron spin relaxation in solvated Mn(II) ions in DMF and dimethylsulfoxide (DMSO), using Mn(ClO₄)₂, Garrett and Morgan ¹³ reported the characteristic six line hyperfine spectrum for the Mn(II) ion. Lohmann et al. ¹³ using MnCl₂ in these same solvents, reported an EPR spectrum for Mn(II) in which the two outer peaks were split to give an eight line spectrum and a reduction in intensity, which was attributed to the influence of the methyl groups of the solvent molecules. The purpose of the present work is to show that the difference in these reported spectra is due to the formation of Mn(II)-chloro complexes, and to demonstrate the applicability of EPR spectroscopy to the study of such complexes. DMF was the solvent chosen for this study since optical spectroscopic...
scopic work by Pflaum and Popov\textsuperscript{14} indicated the presence of Mn(II)-chlo ro complexing.

**Experimental**

*Materials.* Mn(ClO$_4$)$_2$·6 H$_2$O, obtained from G. F. Smith Chemical Company was dried under vacuum over P$_2$O$_5$ before use. Anhydrous MnCl$_2$ was purchased from K & K Laboratories. The CsCl was optical grade powder from the Harshaw Chemical Company, and Mallinckrodt spectral grade DMF was used as received. Eastman tetramethylammonium chloride was used at high chloride concentrations. All other solvents were reagent grade.

*Apparatus.* A Varian V4500 100-kHz EPR spectrometer operating in the X-band region near 9.5 GHz was used. The sample temperature was varied using a Varian V4547 variable temperature accessory by which the sample temperature could be held to ±2 °C. The magnetic field sweep was calibrated using a Harvey-Wells proton resonance probe and frequency counter. Manganese concentrations were determined using a Perkin-Elmer Model 303 atomic absorption spectrophotometer.

*Experimental Procedure.* A stock solution of Mn(ClO$_4$)$_2$·6 H$_2$O in DMF was prepared by weighing out the proper amount of solute into a volumetric flask and adding DMF to the mark. The concentration of Mn(II) in solution was determined by atomic absorption analysis using MnCl$_2$ as a standard. Depending on the amount of chloride ion desired, various quantities of CsCl or (CH$_3$)$_4$NCI were weighed into volumetric flasks to which a constant aliquot of the Mn(ClO$_4$)$_2$ solution was added. After the chloride was dissolved by heating, the solutions were allowed to cool and then diluted to the mark with DMF. Using a syringe, a small quantity of each solution was withdrawn, placed into a 1-mm. i.d. quartz capillary tube and sealed. The spectra were recorded as the first derivative of the absorption curve. The peak height for each of the six peaks were taken to be the vertical distance between the maximum and the minimum amplitude of the derivative. 2,2'-diphenyl-1-picrylhydrazyl was used as a reference to measure the $g$-values.

**Results and Discussion**

Mn(ClO$_4$)$_2$, when dissolved in DMF gave a clear, colorless solution. The signal intensity increased over the temperature range 25 – 116 °C, and the line width of the fourth line from low field was found to decrease with increasing temperature. The line width data are in good agreement with the data of Garrett and Morgan\textsuperscript{12}.

Experimentally, three different spectra (Fig. 1) were observed depending on the concentration of added chloride. The appearance of the spectrum as shown in Fig. 1-A is obtained when chloride ion is absent, present at much less than, or even near a 1 : 1 ratio with Mn(II), and addition of chloride converts it into 1-B, which is then converted into 1-C by further addition of chloride. It is evident that 1-A is the spectrum of Mn(II) and 1-C is the spectrum of a Mn(II)-chlo ro complex, while 1-B is simply a mixture of two species and is also the spectrum obtained when MnCl$_2$ is dissolved in DMF. The appearance of the spectrum at very low chloride concentration shows little evidence of the complex, but it is present as seen from the changing peak height of the spectra in Fig. 2. This decrease in peak height as evidence of the formation of a complex with Mn(II) ions was used by Atkinson and Baumann\textsuperscript{15}, and McGarvey\textsuperscript{16} to show the formation of a complex between Mn(II) ions and pyridine in aqueous solution.


\textsuperscript{15} G. Atkinson and J. E. Bauman, Inorg. Chem. 2, 64 [1963].

\textsuperscript{16} B. R. McGarvey, J. physic. Chem. 61, 1232 [1957].
The EPR spectrum of a dilute solution of Mn(II) in DMF (1-A) appears as six hyperfine lines due to coupling of the S = 5/2 electron spin with the I = 5/2 nuclear spin of the Mn²⁺ ion. The hyperfine coupling constant A is taken to be 95 gauss. The species is Mn(DMF)₆²⁺ and is considered octahedral due to similarity of the spectrum of Mn²⁺ in water.

For the Mn(II)-chloro complex (1-C), a contraction of the spectrum is observed and the value of A is taken to be 80 gauss, the interval between the third and fourth lines of the spectrum. This value of A is in good agreement with MnCl₄²⁻ complexes in other solvents. The simplest explanation of the reduced value of A in the complex is that the unpaired electrons are delocalized on to the chloride ions of the complex and result in decreased interaction with the Mn nucleus. Thus the Mn hyperfine spacing is less than would be expected for no electron delocalization.

To ascertain the nature of the complex present in solution, the mole ratio method was used. Using this method, two experiments were carried out. In the first, the concentration of the manganese was held constant and varying amounts of chloride ion were added. The total peak height for Mn(II) per unit signal level was plotted against the ratio moles Cl⁻/moles Mn(II). The source of the Mn(II) was Mn(ClO₄)₂, since the perchlorate anion is virtually noncomplexing. The chloride was introduced as CsCl for [Cl⁻] < 3.0 and as (CH₃)₄NCI for higher concentrations of Cl⁻. Duplicate measurements were made with both CsCl and (CH₃)₄NCI between [Cl⁻]/[Mn²⁺] ratios of 2 and 3 to assure that the two chlorides had the same effect. The effect of changing the ratio of chloride to Mn(II) ions on Mn(II) peak height is illustrated in Fig. 2. The presence of the inflection point at a Cl⁻/Mn(II) ratio equal to 1 shows that the species MnCl⁻ is present in addition to the Mn(II) ions. The minimum values of total values of peak height in the [Cl⁻]/[Mn²⁺] range of 1 to about 3 could indicate further complexes, but the data is not sufficient to infer this. The region of minimum intensity from [Cl⁻]/[Mn²⁺] = 1 – ~ 3.5 was also found by Levanon in methanol. The inflection point at [Cl⁻]/[Mn²⁺] = 4 indicates a tetrachloro complex (MnCl₄²⁻) similar to that found by Chan et al. in acetonitrile. In the second experiment, the concentration of chloride ion was held constant and the Mn(II) concentration varied. A 1 : 1 complex was also determined from a mole ratio plot of Mn(II) peak height vs. moles Mn(II) per unit signal level per unit amplitude.

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### Table 1. EPR data for Mn(II) in 1,4-Dimethylformamide at various chloride concentrations at 25°, 48° and 116°C using CsCl. a Mn(ClO₄)₂ at 1.42 \times 10^{-3} \text{m} in each case.

<table>
<thead>
<tr>
<th>Moles Cl⁻ \times 10^{-3}</th>
<th>Moles Mn(II) \times 10^{-3}</th>
<th>Total peak height per unit signal level per unit amplitude \times 10^{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>79.0</td>
</tr>
<tr>
<td>1.34</td>
<td>0.183</td>
<td>60.0</td>
</tr>
<tr>
<td>3.00</td>
<td>0.417</td>
<td>46.9</td>
</tr>
<tr>
<td>4.53</td>
<td>0.629</td>
<td>30.8</td>
</tr>
<tr>
<td>6.44</td>
<td>0.894</td>
<td>16.2</td>
</tr>
<tr>
<td>8.15</td>
<td>1.13</td>
<td>9.7</td>
</tr>
<tr>
<td>10.0</td>
<td>1.39</td>
<td>4.7</td>
</tr>
<tr>
<td>15.2</td>
<td>2.11</td>
<td>1.4</td>
</tr>
<tr>
<td>19.9</td>
<td>2.76</td>
<td>0.92</td>
</tr>
</tbody>
</table>

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### Table 2. EPR data for Mn(II) in 1,4-Dimethylformamide at constant chloride concentration at 25°, CsCl at 1.42 \times 10^{-3} \text{m} in each case.

<table>
<thead>
<tr>
<th>Moles Mn(II) \times 10^{-3}</th>
<th>Moles Cl⁻ \times 10^{-3}</th>
<th>(Total peak height/unit signal level/unit amplitude) \times 10^{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.909</td>
<td>0.640</td>
<td>.56</td>
</tr>
<tr>
<td>1.45</td>
<td>1.02</td>
<td>3.15</td>
</tr>
<tr>
<td>1.82</td>
<td>1.28</td>
<td>8.24</td>
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<tr>
<td>2.36</td>
<td>1.66</td>
<td>12.7</td>
</tr>
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<td>2.73</td>
<td>1.92</td>
<td>15.0</td>
</tr>
<tr>
<td>4.91</td>
<td>3.45</td>
<td>39.3</td>
</tr>
<tr>
<td>7.09</td>
<td>4.99</td>
<td>63.9</td>
</tr>
</tbody>
</table>

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18 J. H. Yoe and A. L. Jones, Analytic. Chem. 16, 111 [1944].
data from this system. The data for these systems are presented in Tables 1 and 2. In previous investigations of chloride complexes of Mn(II), the MnCl\(^{0}\) ion has been shown to exist in water-alcohol mixed solvents\(^7\) as well as in aqueous solution\(^3\). STEWART and WEAR\(^9\) have observed the MnCl\(^{0}\) species in DMF spectrophotometrically.

Any species with one-three chlorides attached to the Mn(II) apparently are unsymmetrical, and therefore, do not produce an EPR spectrum. The MnCl\(^{4}\) species has cubic symmetry which accounts for the narrowing of the line width. This complex would be expected to have a higher intensity\(^1\), but it apparently is never the only species. The continuous increase in intensity to \([\text{Cl}^{0}] / [\text{Mn}^{2\circ}] \approx 7.0\) also indicates more and more MnCl\(^{4}\) is being formed from lower chloro species. In other solvents, the intensity has been higher than that of the perchlorate solution\(^10,11\).

**Thermodynamic Data.** Only the MnCl\(^{0}\) species was studied as a function of temperature because of difficulties of working at higher chloride concentrations. The data at higher chloride concentration was also less reliable than the region near a \(1:1\) ratio of \([\text{Mn}^{2\circ}] / [\text{Cl}^{0}]\).

The reaction of Mn\(^{2\circ}\) with Cl\(^{0}\) in DMF at lower \([\text{Mn}^{2\circ}] / [\text{Cl}^{0}]\) is postulated as follows:

\[
\text{Mn}^{2\circ} + \text{Cl}^{0} \rightleftharpoons \text{MnCl}^{0}. \tag{1}
\]

The Mn\(^{2\circ}\) and MnCl\(^{0}\) species presumably contain solvent molecules in the first coordination sphere. The equilibrium constant for the above reaction is given by

\[
K_c = \frac{[\text{MnCl}^{0}]}{[\text{Mn}^{2\circ}][\text{Cl}^{0}]} = \frac{\gamma_{\text{MnCl}^{0}}}{\gamma_{\text{Mn}^{2\circ}} \gamma_{\text{Cl}^{0}}} \approx \frac{[\text{MnCl}^{0}]}{[\text{Mn}^{2\circ}][\text{Cl}^{0}]}, \tag{2}
\]

where the activity coefficients have been assumed to be near unity, in view of the low ionic strength of the solutions. (\(\mu \approx 0.02\) for a ratio below 3.)

Determination of the Mn(II) concentrations from the EPR spectra were based on the intensity of the uncomplexed Mn(II) signal. Although the hyperfine components of the Mn(II) spectrum are not exactly Lorentzian in shape, their intensities may be considered proportional to the height of the derivative curve times the square of its width. Since a number of the observed EPR spectra in this study are due to more than one paramagnetic species, the individual line widths cannot be measured. However, the intensity as measured by summing the heights of the six hyperfine lines gave a linear plot against concentration over the range of \(1 \times 10^{-3}\) to \(7.2 \times 10^{-3}\) m at each temperature used in this study. The uncomplexed Mn(II) concentrations were read directly from each calibration plot. By calibrating in this manner, we have compensated for line width variation due to temperature; however, intensity measurements of this sort on the sample solutions could be affected by line width variation due to added Cl\(^{0}\), enhancing the error in determining the Mn(II) concentrations. HAYES and MYERS\(^6\) have shown that in aqueous solution, below 80 °C the effect of added Cl\(^{0}\) on the line width of the \(M_{I}=+1/2\) component is less than 0.1 Oe up to 0.1 m Cl\(^{0}\), and indicate that in the Cl\(^{0}\) concentration range used in this study (0 to \(2.0 \times 10^{-2}\) m), line widths would not be greatly affected below 140 °C. Therefore, the effects of added Cl\(^{0}\) on the EPR intensity measurements in this study are believed to be negligible.

Since \([\text{MnCl}^{0}] = [\text{Mn}^{2\circ}]_0 - [\text{Mn}^{2\circ}]_1\) and \([\text{Cl}^{0}] = [\text{Cl}^{0}]_0 - [\text{MnCl}^{0}]\) (where the subscript refers to initial concentrations), an equilibrium constant, \(K_c\), can be calculated for (1). In Fig. 3, log \(K_c\) vs. \(1/T\) has been plotted and a straight line fit obtained for the temperature range 25 °C to 116 °C. From the slope of this straight line, \(\Delta H^0\) for the reaction was calculated to be \(-1.20\) Kcal·mole\(^{-1}\). The values for \(K_c\), \(\Delta F^0\) and \(\Delta S^0\) at 25 °C are \(6.457 \times 10^3\), \(-5.20\) Kcal·mole\(^{-1}\), and 13.4 cal·mole\(^{-1}\) deg\(^{-1}\) respectively.

**g-values.** The g-values for Mn\(^{2\circ}\) and MnCl\(^{0}\) in DMF were determined to be the same within ex-
perim ental erro r (2.003 ± 0.002) by com parison
with 2,2-diphenyl-1-picrylhydrazyl.

Spectra in Other Non-Aqueous Solvents. The
EPR spectrum of anhydrous MnCl$_2$ in dimethylsulfoxide, ($\varepsilon = 48.9$) acetonitrile, ($\varepsilon = 37.5$) nitrobenzene ($\varepsilon = 36.1$) and nitromethane ($\varepsilon = 39.4$) was
also investigated. As reported by LOHMANN$^{13}$,
MnCl$_2$ in dimethylsulfoxide gave much the same
spectrum as in DMF. The intensity of the Mn(II)-
chloro complex spectrum could be increased by the
addition of chloride ion. Unfortunately, the solubi-
licity of MnCl$_2$ in the latter three solvents is too low
to obtain well defined spectra, however, addition of
excess chloride ion appears to change the spectra to
ones that are qualitatively similar to that obtained
in DMF. The spectra are not discussed individually
since they are sufficiently alike to indicate the for-
mation of a Mn(II)-chloro complex.

Conclusions

Three different spectra can be shown for solu-
tions of Mn(ClO$_4$)$_2$ in DMF to which chloride ion
has been added, and the presence of MnCl$_{10}^+$ and
MnCl$_{42}^+$ have been demonstrated by a mole ratio
plot. It has been shown that the same species appear
when MnCl$_2$ is dissolved in DMF. The reported
spectrum of MnCl$_2$ in DMF solution can thus be
explained in terms of co-existence of the species
Mn$^{2+}$ and MnCl$_4^{2-}$. The decrease in intensity of
the spectrum is due to the MnCl$^{2+}$ species that does not
produce a signal.

The EPR spectra of MnCl$_2$ in solvents with high
dielectric constants (Formamide, $\varepsilon = 109$; water,
$\varepsilon = 79.8$) do not show a Mn(II)-chloro complex
spectrum$^{13}$ thus supporting an equilibrium lying to
the left for (1). However, a Mn(II)-chloro complex
is formed in solvents of dielectric constant between
36 and 50 indicating that the solvent dielectric
constant influences the position of the equilibrium.

As expected for S-state ions, $g$-values are close to
2.0023, the value for the free electron.

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