On the Red Intermediate in a Photochemical Reaction of the Mo(CN)$_8^{4\circ}$ Ion

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There is a disagreement in the literature as to the intermediates and final products of the photochemical reaction of diluted aqueous solutions of K$_2$Mo(CN)$_8$. In the article we give arguments to support our view that the formula of the red intermediate ion is [Mo(CN)$_8$(H$_2$O)$_2$]$^{4\circ}$. In particular we give an answer to recent objections by P e r u m a r e d d i against such an interpretation. In the theoretical part we also reconsider König's interpretation of the electronic spectrum of [Mo(CN)$_8$]$^{4\circ}$, in terms of a flattened Archimedean antiprism.

The photochemical reaction of diluted aqueous solutions of K$_2$Mo(CN)$_8$ is known to run in at least two different stages. In the first stage a red intermediate is formed which on further irradiation changes into a blue product. Unfortunately there is a disagreement as to the nature of both, the intermediate and the final product. In the present note we are going to discuss the nature of the red intermediate.

According to our opinion[1], based on experiments carried out in pure aqueous solutions as well as in solutions containing NH$_3$ or N$_2$H$_4$, the red intermediate anion has the formula [Mo(CN)$_7$(X)$_2$]$^{4\circ}$, where X = H$_2$O, NH$_3$ or N$_2$H$_4$. Some other authors[2], which investigated the pure aqueous solutions only, assume the intermediate to be a heptacyanide anion, [Mo(CN)$_7$(H$_2$O)$_2$]$^{3\circ}$ or [Mo(CN)$_7$(OH)$_2$]$^{4\circ}$. In two recent articles[3] Perumareddi has hoped to give serious arguments against our interpretation and in favour of the other one. We will recapitulate our arguments in short and show that Perumareddi’s arguments are by far not so convincing and unequivocal as claimed.

Our arguments for the [Mo(CN)$_8$(H$_2$O)$_2$]$^{4\circ}$ structure are as follows:

1) Dealing with irradiated solutions we have been able to isolate complexes of the type MeMo(CN)$_8$X$_2$·4 H$_2$O, where Me = Cd or Mn(II), X = NH$_3$ or N$_2$H$_4$. Hence one could well expect by analogy that the aqua complex has the same form.

2) The electronic absorption spectrum of the [Mo(CN)$_8$(NH$_3$)$_2$]$^{4\circ}$ and [Mo(CN)$_8$(N$_2$H$_4$)$_2$]$^{4\circ}$ anions[1] appears to be very similar to that of irradiated aqueous solutions, published by Ad a m s o n and Perumareddi[4] (Fig. 2 of ref. 1.c. 3a). This suggests a similar structure of all above complexes.

3) Our very recent investigations on the resistance changes of the solutions in the course of irradiation suggest the same conclusion. In the first stage of irradiation an increase of resistance is observed in all the cases, as shown in Fig. 1 (taken from ref. 1.c. 1b) 4. This increase might result from the naturally expected lower mobility of the red [Mo(CN)$_8$X$_2$]$^{4\circ}$ ions than that of [Mo(CN)$_8$]$^{4\circ}$. The results support the reasoning by analogy.

4) Our arguments are valid, if ions of the type [Mo(CN)$_8$(NH$_3$)$_2$]$^{4\circ}$ or [Mo(CN)$_8$(N$_2$H$_4$)$_2$]$^{4\circ}$ do really exist. A direct proof of their existence was given, in a sense, under i. An indirect proof follows

References on this subject can be found in the papers 1.c. 1b, 3b, 4.


4) The right part of the curves corresponds to a continued irradiation and is related to the subsequent photochemical reaction.

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to some extent from Table I. One can see from the Table that the spectra of \([\text{Mo(CN)}_8]^{4-}\) and the red intermediate \([\text{Mo(CN)}_8(\text{NH}_3)_2]^{4-}\) are very similar. The positions of all the maxima are almost the same except of the lowest singlet-singlet transition, in which case they differ by 2.5 kK (this is slightly more than a difference of two subsequent states of the \(\text{CN}^-\) stretching vibration mode). We expect the two additional ligands \(\text{NH}_3\) to lie in an outer coordination sphere; therefore their influence on the spectrum should be small. It would be rather difficult to understand the similarity if the red intermediate had had the form \([\text{Mo(CN)}_7(\text{NH}_3)]^{3-}\), particularly as \(\text{CN}^-\) and \(\text{NH}_3\) ligands lie in the spectrochemical series far apart.

Let us reconsider now the arguments which have been risen against our interpretation and which seem to support the heptacyanide concept.

i) Perumareddi hopes to have shown that the photolysis runs in accordance with the scheme

\[
[\text{Mo(CN)}_8]^{4-} \xrightarrow{\text{hv}} \text{R} + \text{CN}^- \quad (1)
\]

\[
\text{R} \rightarrow \text{blue terminal product} \quad (2)
\]

where \(\text{R}\) is the red intermediate. His decisive argument follows from the iodometric titration of the irradiated solutions. However, he seems not to take into account that from the very beginning of irradiation together with the red intermediate also the blue terminal product is formed (it follows e.g. from Figs. 1 and 2 of ref. 1 c. 3a). The formation of this product, which is a hydroxotetracyanide complex, is associated with a release of four \(\text{CN}^-\) ions. Moreover, the hydroxotetracyanide anion, say for example of formula \([\text{Mo(CN)}_4(\text{OH})_3(\text{H}_2\text{O})]^3\text{–}\), is quantitatively oxidized by iodine. Thus the overall

<table>
<thead>
<tr>
<th>Maxima observed for</th>
<th>Electronic transitions calculated for</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mo(CN)}_8]^{4-})</td>
<td>([\text{Mo(CN)}_8(\text{NH}_3)_2]^{4-})</td>
</tr>
<tr>
<td>(\text{König's antiprism})</td>
<td>(\text{flattened antiprism})</td>
</tr>
<tr>
<td>no</td>
<td>2.0 (3\text{E}_2)</td>
</tr>
<tr>
<td>no</td>
<td>9.5 (1\text{E}_2)</td>
</tr>
<tr>
<td>17.2 (\text{ST})</td>
<td>17.5 (3\text{E}_3)</td>
</tr>
<tr>
<td>19.6 (\text{SS})</td>
<td>19.5 (3\text{A}_2)</td>
</tr>
<tr>
<td>23.4 (\text{SS})</td>
<td>23.3 (1\text{E}_3)</td>
</tr>
<tr>
<td>24.0 (1\text{B}_1, 1\text{B}_2)</td>
<td>27.1 (1\text{A}_1, 3\text{E}_1)</td>
</tr>
<tr>
<td>27.2 (\text{SS})</td>
<td>27.3</td>
</tr>
<tr>
<td>32.9 (\text{SS})</td>
<td>32.6</td>
</tr>
<tr>
<td>37.4 (\text{SS})</td>
<td>37.4</td>
</tr>
</tbody>
</table>

Table I. Calculated and observed absorption spectra of \([\text{Mo(CN)}_8]^{4-}\) and \([\text{Mo(CN)}_8(\text{NH}_3)_2]^{4-}\) (in kK).
process can be expressed by the equation:

$$[\text{Mo(CN)}_4(\text{OH})_3(\text{H}_2\text{O})]^3\overset{3}{\overset{3}{\alpha}} + 4 \text{CN}^\alpha + 9 \text{J}_2 + 5 \text{OH}^\alpha \rightarrow \text{MoO}_4^{2\alpha} + 8 \text{JCN} + 10 \text{J}^1 + 5 \text{H}_2\text{O}.$$  (3)

We see that the blue product consumes appreciable amounts of iodine, by an order of magnitude more than expected in the case of the red one, the ratio being 9:1. Hence the titration results quoted by Adamson and Perumareddi are far from being as unequivocal an argument as could follow from their article.

ii) A second severe argument is given by the statement that the red intermediate disappears in the dark quicker when CN\(^\alpha\) is added and \(p_{II}\) is decreased. First of all we have some comments to the way in which their experiments have been performed. The buffer was added to a solution of octacyanide before the irradiation. However, the run of this photochemical reaction depends strongly on \(p_{II}\) of the solution and for different \(p_{II}\) values varying amounts of both, red and blue products are obtained. Therefore we have some doubt as regards the validity of eq. 3 of ref. l.c. 3a, which gives the influence of \(p_{II}\) on the reverse reaction of the red intermediate, particularly as the experiments were carried out in a small range of \(p_{II}\).

Making our own experiments we introduced the buffer and also other ions already to the irradiated solution. We have found that the rate of the reverse reaction depends not only on temperature and \(p_{II}\), but also on the ionic strength of the solution and on the presence of some particular substances. Thus, in borax buffer solution of \(p_{II} = 9.5\), the CN\(^\alpha\) ions undoubtedly speed up the back reaction (argument in favour of eq. 1). However, the SCN\(^\alpha\) ions, on the other hand, retard this process rather strongly. On the other hand, the acetic acid-ammonia buffer of the same \(p_{II}\) retards the back process itself and in this case the influence of added CN\(^\alpha\) is insignificant. We cannot explain these effects at the moment, but undoubtedly the reverse reaction (or reactions) is more complicated than suggested by the authors, particularly as in all cases \(D_{\alpha_{\text{max}}}\) and \(D_{\alpha_{\text{in}}}\) (defined in ref. l.c. 3c) are different.

iii) The model of the [Mo(CN)\(_8\)X\(_2\)]\(^4\alpha\) anion, we suggested, was that of an Archimedean antiprism.\(^{1c,16}\) It has two favoured positions in the outer sphere\(^5\) which could be occupied by two additional ligands. In a theoretical article to this Journal\(^3b\) Perumareddi states firmly that were it so, the complex had to be paramagnetic and not diamagnetic, as observed. Using the crystal field theory he thought to be able to show that for all reasonable distances of the additional ligand, \(R\), and for all reasonable values of the ratio of integrals \(\langle q_2 \rangle\) and \(\langle q_4 \rangle\), defined in his paper, the ground level should be degenerate and hence a \(d^2\) complex should be paramagnetic.

We are not sure if the naive form of the crystal field theory is completely a reliable basis for such a discussion. However, even within the same theoretical framework we can show that Perumareddi’s “unequivocal” argument is rather fictitious. Perumareddi assumed that the antiprism structure follows from twisting of a cube. In fact both, theoretical arguments and experimental results indicate that the eventual antiprism should be flattened, with the \(\Theta\) angle equal approximately to \(60^\circ \pm 1^\circ\) and \(120^\circ \pm 1^\circ\), respectively.\(^5,6\) Let us assume for example that \(\Theta = 60^\circ\) and \(120^\circ\) accordingly. The basic equation 3 of ref. l.c. 3b is now invalid and should be replaced by eq. (4):

\[
E(\{d_{\alpha x} , d_{\alpha y}\}) = -\frac{1}{7} \langle q_2 \rangle_{\text{eff}} + \frac{148}{336} \langle q_4 \rangle_{\text{eff}}
\]

\[
E(\{d^2, d_{\alpha x} , d_{\alpha y}\}) = +\frac{2}{7} \langle q_2 \rangle_{\text{eff}} - \frac{37}{336} \langle q_4 \rangle_{\text{eff}}
\]

\[
E(\{d_{\alpha x} \}) = -\frac{2}{7} \langle q_2 \rangle_{\text{eff}} - \frac{222}{336} \langle q_4 \rangle_{\text{eff}}
\]

where

\[
\langle q_2 \rangle_{\text{eff}} = \langle q_2 \rangle - 2\langle q_4 \rangle; \quad \langle q_4 \rangle_{\text{eff}} = \langle q_4 \rangle - \frac{32}{37} \langle q_4 \rangle'.
\]

Obviously \(\langle q_2 \rangle \gg \langle q_2 \rangle'\) and \(\langle q_4 \rangle \gg \langle q_4 \rangle'\), and hence \(\langle q_4 \rangle_{\text{eff}} \approx \langle q_4 \rangle\), because the \(d\) electrons of the central atom interact definitely more with CN\(^\alpha\) than with H\(_2\)O or generally X. Hence in the more sophisticated flattened antiprism model the role of the two additional ligands in the outer sphere is almost insignificant. The significance of the ligands X found by Perumareddi was due to an oversimplification of the model of the \(D_{4d}\) symmetry.

Perumareddi’s assumption was likely to be based on the fact that the twisted cube model was used with some success by Gliemann and König\(^7\) to interpret the electronic spectrum of Mo(CN)\(_8\)\(^4\alpha\). How-


ever, four years ago one of us (A.G.) tried to take into account the flattening effect within the framework of König’s theory. It was found that for \( \langle q_2 \rangle \sim 4 - 5 \langle q_4 \rangle \) an Tanabe-Sugano diagram is obtained which can be used with some success to interpret the spectrum. The diagram is given in Fig. 2 and the comparison of calculated and observed energies is given in Table I.

One can see from the Table that the flattened antiprism leads to almost the same agreement with experiment as the cubic antiprism of König and Gliemann. Now, however, the assignment of transitions is completely different and there is no predicted triplet state at about 2 kK and no predicted singlet state at about 9.5 kK, two strange results of König’s theory which had been strongly attacked in the past. However, the theory does not predict or predicts wrong the position of the S–T band at 17.2 kK. But this is a very weak band the position of which is in our opinion not certain.

The values given in Table I have been found for \( C = 4 B, \quad B = 525 \text{ cm}^{-1}, \quad D_s = \frac{1}{2} \left( 30 \cos^2 \Theta - 35 \cos^4 \Theta - 3 \right) \langle q_4 \rangle, \quad D_s/B = 1.95, \quad D_{t} = \frac{a}{3} (1 - 3 \cos^2 \Theta) \langle q_2 \rangle = 20/3 D_s. \) If \( \Theta = 60^\circ \), then \( \langle q_2 \rangle = 47,600 \text{ cm}^{-1}, \) and \( \langle q_4 \rangle = 9,300 \text{ cm}^{-1}. \) The ratio of \( \langle q_2 \rangle \) to \( \langle q_4 \rangle \) is then slightly high, but not impossible so.

The numerical value of \( \langle q_4 \rangle \) seems to be low but taking into account the fact that the eight charged ligands coordinated around the central atom might be well a little farther than in the case of six charged ligands in a \( O_h \) complex and that the antibonding properties of appropriate orbitals are likely to be smaller in the case of the \( D_{4d} \) symmetry than in the case of \( O_h \) symmetry, such an eventuality cannot be excluded.

As already mentioned, these calculations have been carried out with the standard ratio \( C = 4 B. \) However, it was pointed out that in the case of cyanides a ratio \( C = 7 B \) is more appropriate. It is likely that with this modified ratio our results of calculations could be still improved. And certainly a still more reliable interpretation of the spectrum would be possibly obtained with the help of the molecular orbital based ligand field theory. We think, however, that the discussion presented shows sufficiently clearly the inadequacy of Perumareddi’s theoretical objection.

