# Temperature Dependence of 10*Dq* for Aqueous Hexaaquomanganese(II)

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The d → d electronic transitions of $Mn(H_2O)_6^{2+}$(aq) were studied over the temperature range of 25–250 °C in a solution of the perchlorate salt. The crystal field parameter 10*Dq* was found to decrease by about 1000 $cm^{-1}$ while the Racah interelectronic repulsion parameters *B* and *C* remained fixed with increasing temperature. The Mn–O bond distance was found to increase by 3 ± 1% over the temperature range studied.

## Introduction

Understanding the properties of transition metal ions in hot aqueous solutions is of considerable geochemical significance. Geochemical processes such as the formation of ore deposits from hydrothermal fluids or the interaction between sea water and the effluent from hot springs at midocean ridges can only be adequately modeled or explained using relevant thermodynamic data for these ions. In many cases, solubilities of various phases are affected by the relative stabilities of dissolved complexes and cannot be predicted adequately by extrapolation of low-temperature properties.

One of the most convenient methods for measuring the concentration of a chemical species in solution is absorption spectroscopy. Since the absorption spectrum of a metal complex in aqueous solution varies in energy and intensity as temperature and pressure are changed, one needs to know this variation in order to use the spectrum to measure concentration under different conditions.

In the present study, we have recorded the spectrum of $Mn(H_2O)_6^{2+}$(aq) from 25 to 250 °C; this is the only species present in this temperature interval in our solution. The spectrum is characterized by standard crystal field parameters, and their temperature dependencies are determined. The results of this study will be used in the analysis of spectra of aqueous chloride solutions where various chloro complexes of $Mn^{2+}$ are also present in addition to the hexaaquo species. (See refs 1–5 for related work.)

## Experimental Section

A solution, approximately 0.9 M, was prepared by dissolving $Mn(ClO_4)_2{\cdot}6H_2O$ (Johnson Matthey Aesar Chem. 12309) in 0.01 M $HClO_4$ made with doubly deionized water. Titanium cells with unoriented sapphire windows as described in ref 6 were used. The Helicoflex seals described therein were replaced with Teflon o-rings to avoid copper contamination of the sample. The cell pathlength was 0.80 ± 0.05 cm. Degassed solution was introduced into the cells under vacuum to prevent bubble formation.

All measurements were performed using the spectrophotometer and other equipment described in ref 4 with the temperature controller detailed in ref 6. Absorbance values were read at 0.5-nm intervals for each spectrum. The base-line correction was determined at 25 °C with water in both the sample and reference beams. Spectra were collected at 25 °C intervals as the temperature was raised and then checked for reproducibility at the same temperature as the cells cooled.

## Results and Discussion

Manganese(II) exists as the hexaaquo ion in acidic solutions of $Mn(ClO_4)_2{\cdot}6H_2O$ since water, which is present in an overwhelming abundance, is the best ligand available for the metal ion. Also, divalent manganese has a rich d → d spectrum that is strikingly sensitive to change in its coordination sphere. It is especially noteworthy that all of the spectra shown in Figure 1 possess a single sharp transition at 25 000 $cm^{-1}$. Previous spectroscopic studies, where complexes such as $Mn(H_2O)_5Cl^+$ or other manganese species are also present in solution, all show an additional sharp peak in the spectrum for each different type of manganese complex.[7,8]

The 25 °C spectrum corresponds to what has been reported previously by Heidt et al.[9] Between 16 000 and 31 000 $cm^{-1}$, convenient limits for our discussion, there are five spin-forbidden bands all originating from the $^6A_{1g}$(S) ground state:

| excited state | observed peak max ± spectral band width ($cm^{-1}$) |
|---|---|
| $^4T_{1g}$(G) | 18 850 ± 6 |
| $^{T}{}_{2g}$(G) | 23 100 ± 13 |
| $^4A_{1g}$(G),$^4E_g$(G) | 25 000 ± 21 (25 280 shoulder) |
| $^4T_{2g}$(D) | 28 050 ± 40 |
| $^4E_g$(D) | 29 810 ± 44 |

As the temperature is increased, the T bands all undergo a gradual blue shift while the sharp A and E bands stay at essentially the same energy.

The A,E(G) band is very sharp and remains obviously located at the same energy from 25 up to 175 °C. At 200 °C, the $T_{2g}$(G) band starts to overlap slightly with this band so that it has a flat top which includes both the 24 969- and 25 000-$cm^{-1}$ data points. The overlap increases along with the temperature leading to an obvious asymmetry and observed A,E(G) band maximum of 24 969 $cm^{-1}$ at 225 and 250 °C. Considering that the low-energy side of this band does not show a red shift and that it is so firmly rooted at a constant energy below 200 °C, we have assumed that this apparent change in the peak position is entirely due to overlap with the $T_{2g}$(G) band.

Transition energies to the A,E(G) and E(D) states are independent of 10*Dq* as can readily be seen from an Orgel or Tanabe–Sugano diagram for a $d^5$ system. Since the observed energies of these bands remain constant over the temperature range, we conclude that the Racah parameters *B* and *C* must also

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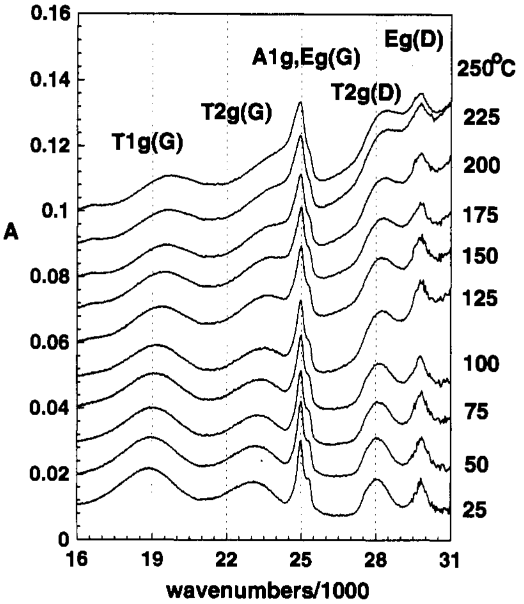

**Figure 1.** Electronic absorption spectra of $Mn(H_2O)_6^{2+}$ in a 0.9 M $Mn(ClO_4)_2$ aqueous solution using 0.85 ± 0.05 cm path length cells from 25 to 250 °C. Spectra are displaced along the absorbance axis for clarity.

**Table 1.** Values of 10*Dq* Calculated Using Eq 1 and the Given Parameters

| | | 10*Dq* (cm$^{-1}$) | | |
|---|---|---|---|---|
| *T* (°C) | obsd energy of the $T_{1g}(G)$ band (cm$^{-1}$) | $\alpha = 65$<br>$B = 817$<br>$C = 3107$ | $\alpha = 76$<br>$B = 839$<br>$C = 3019$ | $\alpha = 90$<br>$B = 867$<br>$C = 2907$ |
| 25 | 18 850 | 7814 | 7632 | 7392 |
| 50 | 18 940 | 7719 | 7537 | 7298 |
| 75 | 18 990 | 7662 | 7484 | 7241 |
| 100 | 19 070 | 7585 | 7400 | 7165 |
| 125 | 19 180 | 7469 | 7283 | 7050 |
| 150 | 19 400 | 7232 | 7050 | 6813 |
| 175 | 19 510 | 7111 | 6934 | 6693 |
| 200 | 19 590 | 7029 | 6849 | 6612 |
| 225 | 19 630 | 6989 | 6809 | 6572 |
| 250 | 19 780 | 6824 | 6647 | 6407 |

be constant. Values for $B$ and $C$ can then be calculated from

$$E_{\mathrm{A,E(G)}} = 10B + 5C + 20\alpha = 25\,000\ \mathrm{cm}^{-1}$$

$$E_{\mathrm{E(D)}} = 17B + 5C + 6\alpha = 29\,810\ \mathrm{cm}^{-1}$$

where $\alpha = 76$ cm$^{-1}$ is Tree's correction.[10] The solutions to these equations are $B = 839$ cm$^{-1}$ and $C = 3019$ cm$^{-1}$. (We have used the 25 000-cm$^{-1}$ peak and dismissed its 25 280-cm$^{-1}$ shoulder in the calculation of these parameters. Clearly, the $A_{1g}(G)$ and $E_g(G)$ states are not exactly degenerate here but this choice is a reasonable, even customary, way to proceed in cases where the two transitions are not completely resolved. The position of the shoulder is not as well defined as that of the sharp peak, especially at higher temperatures. The issue of the splitting of these states is addressed at length in ref 11.)

The observed energy of the $^4T_{1g}(G)$ transition varies with temperature as indicated in Table 1. Even though this band is broad and has a low absorption coefficient, these peak values were determined reliably by close inspection of spectra with an expanded absorbance scale. For all temperatures, the estimated uncertainty in the reported peak maximum does not exceed ± 6 cm$^{-1}$. Using these peak energies along with $B$, $C$, and $\alpha$ discussed above, we can calculate 10*Dq* from the following relationship (see Appendix)

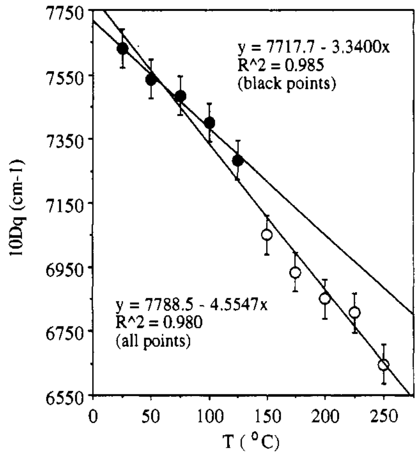

**Figure 2.** Plot of variation in 10*Dq* with temperature for $Mn(H_2O)_6^{2+}$ (aq). Error bars represent the range of values calculated using the extrema of transition energies.

**Table 2.** Comparison of Experimentally Determined $T_{2g}$ Peak Energies and Those Calculated from *B*, *C*, *α*, and 10*Dq* (All Energies Given in cm$^{-1}$)

| | $T_{2g}(D)$ | | | $T_{2g}(G)$ | | |
|---|---|---|---|---|---|---|
| *T* (°C) | obsd | calcd | % diff | obsd | calcd | % diff |
| 25 | 28 050 | 28 170 | –0.4 | 23 100 | 23 020 | 0.3 |
| 50 | 28 090 | 28 188 | –0.3 | 23 200 | 23 075 | 0.5 |
| 75 | 28 120 | 28 199 | –0.3 | 23 260 | 23 140 | 0.7 |
| 100 | 28 150 | 28 217 | –0.2 | 23 390 | 23 151 | 1.0 |
| 125 | 28 250 | 28 242 | 0.03 | 23 530 | 23 215 | 1.3 |
| 150 | 28 280 | 28 294 | –0.05 | 23 670 | 23 338 | 1.4 |
| 175 | 28 310 | 28 320 | –0.04 | 23 750 | 23 398 | 1.5 |
| 200 | 28 400 | 28 340 | 0.2 | 23 870 | 23 441 | 1.8 |
| 225 | 28 490 | 28 350 | 0.5 | | 23 463 | |
| 250 | 28 490 | 28 389 | 0.4 | | 23 541 | |

$$(10Dq)^2 = (10B + 6C + 12\alpha - E)^2 - (C - 8\alpha)^2 - \frac{4(3B + 2\alpha)^2(10B + 5C + 20\alpha - E)}{(19B + 7C + 10\alpha - E)}$$

where $E$ can be taken to be the energy of the $^4T_{1g}(G)$ transition. Resulting 10*Dq* values are listed in Table 1 and graphed versus temperature in Figure 2. It can be seen that 10*Dq* decreases with increasing temperature from 7632 cm$^{-1}$ at 25 °C to 6647 cm$^{-1}$ at 250 °C. The choice of $\alpha = 76$ cm$^{-1}$ is somewhat arbitrary since values ranging from 65 to 90 cm$^{-1}$ are found in the literature.[11] We chose to focus on 76 cm$^{-1}$, the free-ion value, since the ultimate results of our calculations were not particularly sensitive to $\alpha$ (see Table 1) and this value represents a middle ground. For $\alpha = 65$, 10*Dq* ranges from 7814 cm$^{-1}$ at 25 °C to 6824 cm$^{-1}$ at 250 °C while $\alpha = 90$ yields a range of 7392–6407 cm$^{-1}$ for 10*Dq*.

We have used three transitions to determine $B$, $C$, and 10*Dq* over the temperature range studied as described above. To help convince ourselves that this analysis is self-consistent, we can also check to see whether the other two observed transition energies fit these calculated parameters. Observed and calculated energies for transitions to the $T_{2g}(G)$ and $T_{2g}(D)$ states, with the percent difference from the calculated value at each temperature, are given in Table 2 (see the Appendix for the matrix used to calculate these values). Clearly the worst agreement is for the $T_{2g}(G)$ band at temperatures higher than 100 °C. Under these conditions overlap with the A,E(G) band and a sloping baseline due to the tail of a UV band (*vide infra*) cause the $T_{2g}(G)$ maximum to appear at a higher than appropriate energy. If $\alpha$ is varied, the fit can be improved for one band at a time but this procedure generally results in a worse fit for the other band. In general the predicted and observed values agree satisfactorily to within 1%.

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Our parameters and the crystal field model also predict a transition to the $T_{1g}(P)$ state at 32 400 $\text{cm}^{-1}$. We do not observe this transition even at the lower temperatures where interference from the UV band described in the next paragraph should be minimized. Heidt et al.[9] report this low-intensity transition at 32 960 $\text{cm}^{-1}$. Other investigators[12] also show this transition to have an especially low intensity which may explain why it is not evident in our spectra.

At temperatures above 100 °C there is a noticable slope in the high-energy base line. It is evident above 28 000 $\text{cm}^{-1}$ in the 125 °C spectrum and across most of the energy range in the higher temperature spectra. This slope arises from the trailing off of a UV band, centered at 39 500 $\text{cm}^{-1}$, which grows erratically starting at 100 °C. We have investigated the nature of this band and conclude that it may have come from a minor impurity in the perchlorate salt or leached out of the titianium bombs or the seals. The band is not reproducible in other sample cells or with other manganese salts. However, this is our best data in terms of resolution and signal-to-noise ratio so we have chosen to tolerate, and work around, this unimportant limitation. It seems to create only small perturbations of the peak positions used to calculate $10Dq$.

The temperature dependence of $10Dq$ will be a complicated function of the vibrational modes of the complex. Alternatively, $10Dq$ as a function of temperature can be represented by a Taylor series. The best fit straight line shown in Figure 2 has a slope of $-4.6\ \text{cm}^{-1}/°\text{C}$ and could be useful for roughly extrapolating our results to higher or lower temperature. Fitting terms beyond first order is not justified by the quality of the data set. It is worth noting that the five lowest temperature points, which are least effected by interference from the UV band, give a more gradually sloping and more highly correlated line. Possibly the higher temperature data would follow this trend more closely if the sloping base line were corrected. We cannot make such a correction appropriately at this time.

Figure 2 shows error bars of ± 60 $\text{cm}^{-1}$ derived by calculating the range of $10Dq$ using extreme values of possible transition energies to the $T_{1g}(G)$, $A_{1g}$, $E_g(G)$, and $E_g(D)$ excited states with the spectral band width as an estimate of uncertainty in these values. If the distance between actual data points, 0.5 nm, is used to estimate uncertainty for the peak values, these error bars become ± 90 $\text{cm}^{-1}$.

It is possible to use the observed variation in $10Dq$ to estimate the average change in Mn–O bond length, $R$, produced by a change in temperature. From crystal field theory, $10Dq$ is proportional to $1/R^n$ where $n$ is some small number, typically 4–6.[13] The value of the ratio of the bond length at 250 °C to that at 25 °C is given by

$$R_{250}/R_{25} = (10Dq_{25}/10Dq_{250})^{1/n}$$

When $n$ is taken to be 6, as is typical in the case of dipolar ligands, this ratio is 1.023, an increase in the Mn–O bond length of 2.3% on going from 25 to 250 °C. For $n = 4$, the ratio is 1.035 or a 3.5% increase in the bond length. Alternative values of $\alpha$ do not change these results significantly. Thus the ctrystal field expression indicates that the Mn–O bond length increases between 2% and 4% when the temperature increases from 25 to 250 °C. This increase in the average bond length is evidently a result of anharmonicity in the ground-state electronic potential and greater population of more energetic vibrational states at higher temperature.

For comparison, Rodriguez and Moreno[12] found slightly less than 0.5% increase in the Mn–F bond distance in crystals when comparing data from −196 and +25 °C. Certainly the hexaaquo complexes are populating higher vibrational states to a greater extent since the temperatures in this study are more than 200 °C higher. This would accentuate any increase in R due to anharmonicities in the relevant vibrational modes. It is also not unreasonable to think that transitory distortions caused by intermolecular collisions in the liquid phase might cause the observed average increase in bond length to be greater for the complexes in aqueous solution. Tigges and Lehmann[14] concluded that the temperature dependence of the intensities of d → d transitions in many aquo complexes could only be explained in terms of such transient distortions.

It is worth noting that little or no variation in absorption intensity with temperature was observed in this study. The A,E(G) band shows an absorbance maximum of 0.024 in the 25–125 °C spectra. Slight variations observed in other spectra all appear to result from overlap with the $T_{2g}(G)$ band or the increased base-line slope on the high-energy end of the spectrum at higher temperatures, which was discussed previously.

Such a lack of temperature dependence for the intensities of d → d transitions is remarkable since they generally arise via a vibronic mechanism. However, $Mn^{2+}$ is unusual among first-row transition metal ions in that its d → d electronic transitions are not only parity-forbidden in perfect octahedral surroundings, but also spin-forbidden. For these hexaaquo complexes, the mechanism which gives rise to the low intensity of its bands involves spin–orbit coupling and some static odd–parity component of the crystal field. Enderby's neutron diffraction studies[15] show that the $OH_2$ planes do not contain the Mn–O bond direction. The normals to the $OH_2$ planes at the six different ligand positions are undoubtedly uncorrelated at room temperature and above, and therefore produce a field component of odd parity, permitting temperature-independent electric dipole transitions. We are currently investigating this phenomenon in a separate study of appropriate crystals, solutions and glasses over a wider temperature range.

## Summary

Our electronic absorption spectra indicate that $10Dq$ for aqueous hexaaquomanganese(II) decreases from 7632 to 6647 $\text{cm}^{-1}$ over the temperature range 25–250 °C. This corresponds to an increase of approximately 2–4% in the Mn–O bond distance for this octahedral complex. Such changes in the characteristics of each species present in a solution must be accounted for adequately in the analysis of spectroscopic data of transition metal equilibria.

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## Appendix: Matrices for $T_{1g}$ and $T_{2g}$ Transition Energies, Including Tree's Correction, $\alpha$

$T_{1g}$

$$\begin{array}{lll}
10B + 6C + 12\alpha - 10Dq - E & -3\sqrt{2}B - 2\sqrt{2}\alpha & C - 8\alpha \\
-3\sqrt{2}B - 2\sqrt{2}\alpha & 19B + 7C + 10\alpha - E & -3\sqrt{2}B - 2\sqrt{2}\alpha \\
C - 8\alpha & -3\sqrt{2}B - 2\sqrt{2}\alpha & 10B + 6C + 12\alpha + 10Dq - E
\end{array}$$

$T_{2g}$

$$\begin{array}{lll}
18B + 6C + 12\alpha - 10Dq - E & \sqrt{6}B - 2\sqrt{6}\alpha & 4B + C \\
\sqrt{6}B - 2\sqrt{6}\alpha & 13B + 5C + 14\alpha - E & -\sqrt{6}B + 2\sqrt{6}\alpha \\
4B + C & -\sqrt{6}B + 2\sqrt{6}\alpha & 18B + 6C + 12\alpha + 10Dq - E
\end{array}$$

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