# Detection of the Concentration Dependence of Co-ordination to Manganese in Aqueous $MnBr_2$ Solutions by *X*-Ray Absorption Spectroscopy

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Extended *X*-ray absorption fine structure (EXAFS) studies show how the average number of water molecules co-ordinated to manganese in aqueous $MnBr_2$ solutions varies with concentration, implying an equilibrium between species of the type $[MnBr_{(6-n)}(H_2O)_n]^{(n-4)+}$, where $n$ = 4, 5, 6.

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As part of a programme of research by extended *X*-ray absorption fine structure (EXAFS) into the structures of manganese complexes in aqueous and non-aqueous solvents, we recently demonstrated the presence of Mn–Br bonds in aqueous $MnBr_2$ solution.[1] For strong solutions, extra confirmation was obtained by studies at the bromine K-edge, and all the preliminary work suggested that the predominant manganese species present has the stoicheiometry of $[MnBr_2(H_2O)_4]$. We have extended our work to a larger number of samples and developed our computational techniques to obtain reliable estimates of the average number of water molecules co-ordinated to manganese as a function of concentration.

We interpret the changes with concentration to imply an equilibrium between species of the type $[MnBr_{(6-n)}(H_2O)_n]^{(n-4)+}$ where $n$ = 4,5,6; for each concentration, the EXAFS study yields the average number of water molecules $n_{av.}$, that for Br in the complex being $6-n_{av.}$. There is thermodynamic and spectroscopic evidence that only octahedral complexes are present.[2]

EXAFS measurements at room temperature were made at the Synchrotron Radiation Source (SRS) at Daresbury Laboratory using a variety of solution cells and a variety of experimental conditions. Although all spectra were recorded at the manganese K-edge (1.90 Å, 6.54 keV) we used, at different times, transmission and fluorescence detection[3] and both types of monochromatization available: Si(220) with harmonic rejection,[4] and Si(111) with and without double focusing mirror. Our studies showed consistent results for given concentrations regardless of experimental conditions. Solution concentrations studied ranged from saturated solution to dilute solutions of concentration 8—100 mmol $dm^{-3}$. Parallel studies of model compounds were carried out, the most important being on polycrystalline $MnBr_2 \cdot 4H_2O$ which contains[5] monomeric $[MnBr_2(H_2O)_4]$ units, and on the Tutton salt $MnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ which contains[6] the cation $[Mn(H_2O)_6]^{2+}$. Data were reduced using EXAFS programs from the SRS program library.[7] Least squares fitting using UMIST software employed the plane wave approximation.

EXAFS calibration parameters, including corrections to back-scattering and absorber phases were obtained from parallel refinements with the model compounds. A uniformly consistent approach was then adopted to refine the structural parameters of each solution sample [$n_{av.}$, $\Delta r_O$, $\Delta r_{Br}$, photoelectron energy zero and outer (solvent) shell parameters]; thus all the results we report here were derived from similar calculations. The data-range employed was restricted to the EXAFS region with $E > 2.5$ Hartree (1 Hartree = 27.2 eV); $E$ is the photoelectron energy above threshold.

Figure 1 shows the differences between the EXAFS $\chi$-curves for the principal model compounds and selected solutions. It illustrates the trend in the solution spectra as $n_{av.}$ varies between four in polycrystalline $MnBr_2 \cdot 4H_2O$ to six in the Tutton salt. Note, for instance, the beating of the Mn–O and Mn–Br distances in curve (b). Figure 2 shows how $n_{av.}$ varies with concentration. The random errors in the $n_{av.}$ values from the least-squares refinements are shown by error bars. We estimated a further systematic error of about ±0.1 which might move the *whole* curve up or down and which arises from the calibration procedures. If a straight line is fitted through the points shown in Figure 2 its form is given by $n_{av.} = 5.58 - 0.138\,\text{M}/\text{mol dm}^{-3}$ where M is the molarity of the solutions.

We note that although $[MnBr_2(H_2O)_4]$ is present in stronger solutions, saturation is reached before all the $Mn^{II}$ exists in this form. Also, $[Mn(H_2O)_6]^{2+}$ is not the only Mn species present in dilute solutions. The point on Figure 2 for $n_{av.}$ = 5 gives the molarity (M ~4.25 mol $dm^{-3}$) where the concentrations of $[MnBr_2(H_2O)_4]$ and $[Mn(H_2O)_6]^{2+}$ are equal. Preliminary equilibria calculations suggest that a similar concentration of $[MnBr(H_2O)_5]^+$ is present at M ~4.25 mol $dm^{-3}$,

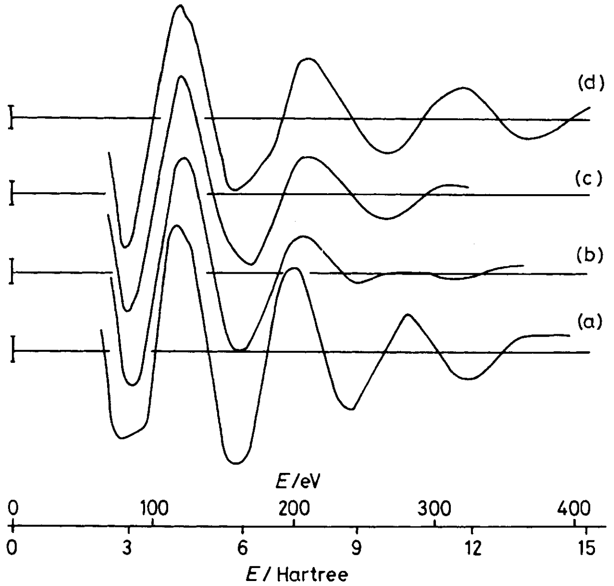

**Figure 1.** Smoothed $\chi$-curves. (a) $MnBr_2 \cdot 4H_2O$; (b) 5 mol $dm^{-3}$ $MnBr_2$ solution; (c) 1.6 mol $dm^{-3}$ $MnBr_2$ solution; (d) $[Mn(H_2O)_6]^{2+}$ as in Tutton salt. Vertical scale markings represent 0.01.

supporting earlier thermodynamic and spectroscopic evidence that all three species are present in the solutions.[2] We also found no evidence for $Br^-$ ions in the solvent shell near the cations.

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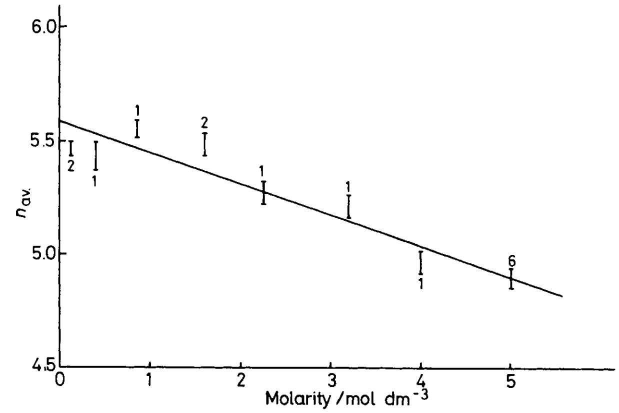

**Figure 2.** Average number $n_{av.}$ of water molecules co-ordinated to $Mn^{II}$ in aqueous $MnBr_2$ solutions as a function of molarity. The number of experimental data sets contributing to each point is indicated.

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