Detection of Mn–Br Bonds in Aqueous $MnBr_2$ Solution by *X*-Ray Absorption Spectroscopy

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Extended *X*-ray absorption fine structure (EXAFS) studies show that the predominant manganese species in aqueous $MnBr_2$ solution has the stoicheiometry of $[MnBr_2(H_2O)_4]$.

As part of a programme of research into the structures of manganese complexes in solution, we have examined the extended *X*-ray absorption fine structure (EXAFS) spectra of aqueous $MnBr_2$ solutions at a variety of concentrations.

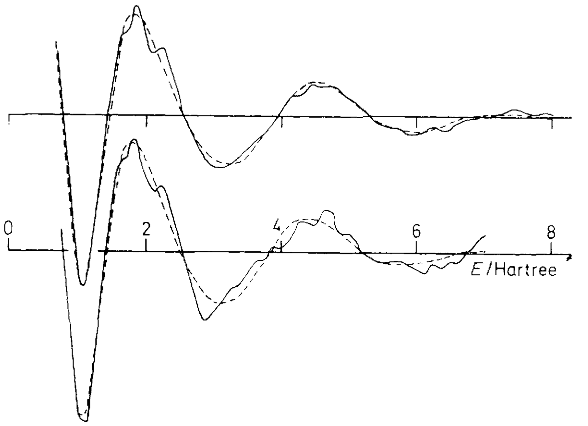

Figure 1. EXAFS χ-curves for saturated $MnBr_2$ solution (upper curves) and 20 mM $MnBr_2$ solution (lower curves). Solid lines: experimental curves; dashed lines: calculated curves (Mn–O + Mn–Br, only).

Measurements were made at room temperature using sample cells with Mylar windows. The EXAFS data were recorded at Daresbury Laboratory using the Synchrotron Radiation Source (SRS). Spectra at the Mn *K*-edge (1.90 Å, 6.54 keV) were recorded in transmission using Si(220) monochromatizing crystals with harmonic rejection.[1] In addition, spectra of dilute solutions (8—100 mM) were recorded in fluorescence mode, using an array of scintillation detectors. Spectra at the Br *K*-edge (0.92 Å, 13.5 keV) were also recorded.

The observed EXAFS data (Figure 1) extend from <0.7 to >8 Hartree where the ripples begin to merge with the signal noise. We have analysed the data using Fourier transform and curve-fitting techniques, and the results for the first co-ordination shell in saturated $MnBr_2$ solution shown in Figure 2 are typical. In Figure 2, the Fourier transform for this solution is compared with the corresponding curves for polycrystalline model compounds $MnBr_2{\cdot}4H_2O$ and $MnBr_2{\cdot}2H_2O$ whose structures are known.[2,3] The EXAFS data for the model compounds were obtained from powdered samples studied under conditions similar to those mentioned above. The model compounds possess Mn–Br bonds as well as Mn–O bonds, the complex present in the crystals of $MnBr_2{\cdot}4H_2O$ being monomeric $[MnBr_2(H_2O)_4]$.[2] The similarity of the three Fourier transforms in Figure 2 demonstrates that the complex in the solution also has Mn–Br and Mn–O bonds. Bond lengths are similar to those found in the tetrahydrate.

Using our computer programs at UMIST, we have examined the relative numbers of Mn–O and Mn–Br bonds present, by full-matrix least-squares curve fitting calculations based on the original EXAFS χ-curves. With only Mn–O included in the calculations for saturated $MnBr_2$ solution, the conventional residual R obtained was *ca.* 30%; $R = 100\ \Sigma|\Delta\chi|/\Sigma|\chi_{obs}|$. Including Mn–Br bonds reduced this to *ca.* 15% (Figure 1). Refining the relative co-ordination numbers for Mn–O and Mn–Br indicated approximately one Mn–Br bond for every two Mn–O bonds present. Extra evidence was obtained by analysing the data recorded at the Br *K*-edge which identified Mn as the only well-defined back-scatterer around the Br atoms. The Mn *K*-edge data for lower concentrations suggest the persistence of Mn–Br co-ordination down to at least 20 mM.

Both Fourier transform and curve-fitting analyses show that the predominant manganese species present in aqueous $MnBr_2$ solution has the stoicheiometry of $[MnBr_2(H_2O)_4]$; *i.e.* the complex occurring in the solution appears to be the same as that in $MnBr_2{\cdot}4H_2O$, the hydrate which can be crystallized from the solution.

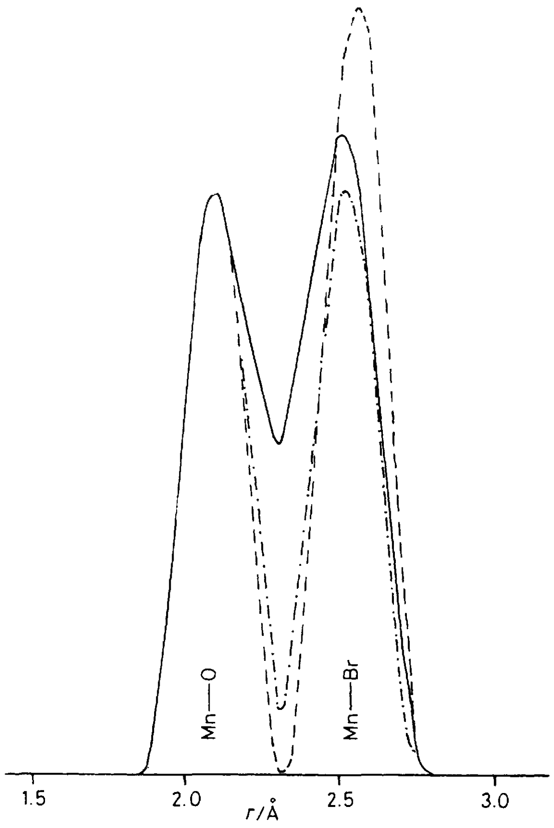

Figure 2. Fourier transforms of EXAFS data showing first co-ordination shell in: saturated $MnBr_2$ solution (——), $MnBr_2{\cdot}4H_2O$ (—·—·—), and $MnBr_2{\cdot}2H_2O$ (– – – – –). Data range 0.7 to >8 Hartree; transforms are scaled to give similar Mn–O peaks.

Galli *et al.*[4] have used EXAFS and other techniques to examine the development of hydration shells in aqueous solutions of $CuBr_2$ and related halide salts. Their findings include the suggestion that such solutions often contain species resembling those present in corresponding crystals. Our results support this general finding, even though we observe different co-ordinational behaviour for $MnBr_2$ solutions.

Our preliminary results for aqueous $MnCl_2$ solutions suggest a behaviour very similar to that for the $MnBr_2$ solutions. For both halide solutions there is also evidence of co-ordination shells beyond the halide and hydration shell characterized above. The information on these outer shells is contained largely in the fine structure near 2 Hartree from the edge (Figure 1). The outer shells appear to be either further shells of water molecules or shells composed (in $MnBr_2$ solutions) from chains of Mn atoms bridged by Br atoms as in crystals of $MnBr_2{\cdot}2H_2O$.

We thank S.E.R.C. for support.

Received, 8th August 1983; Com. 1079

References

1 G. N. Greaves, G. P. Diakun, P. D. Quinn, M. Hart, and D. P. Siddons, *Nucl. Instrum. Methods*, 1983, **208**, 335.
2 K. Sudarsanan, *Acta Crystallogr., Sect. B*, 1975, **31**, 2720.
3 B. Morosin, *J. Chem. Phys.*, 1967, **47**, 417.
4 G. Galli, G. Maisano, P. Migliardo, C. Vasi, F. Wanderlingh, and M. P. Fontana, *Solid State Commun.*, 1982, **42**, 213.